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UNITED STATES  
DEPARTMENT OF THE INTERIOR  
BUREAU OF MINES  
HELIUM ACTIVITY  
DIVISION OF RESEARCH  
INTERNAL REPORT

AN EXPERIMENTAL STUDY OF THE PHASE RELATIONSHIPS

OF A TYPICAL HELIUM CONSERVATION GAS

BY

Lowell Stroud

John E. Miller

L. Warren Brandt

BRANCH Phase Equilibrium and Thermodynamics

PROJECT NO. 1540

DATE July 24, 1959

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## INTRODUCTION

The Department of the Interior recently announced some of the details of a planned program of helium conservation.\* In brief, invitations were extended to private companies to participate in the conservation of helium by financing, building, and operating helium-extraction plants. Helium produced at these plants would be sold on a guaranteed-purchase basis to the Government for storage in underground reservoirs.

On May 24, 1959, two Helium Activity Research Division Reports--No. 8, Thermodynamic Diagrams of Helium-Containing Gaseous Systems I. A Temperature-Enthalpy Chart for Cliffside Gas, by L. W. Brandt and Lowell Stroud; and No. 14, An Experimental Study of the Phase Relationships, Dewpoints, and Compressibility Factors of Keyes Gas, by L. W. Brandt, Lowell Stroud, and Herbert E. Bruce, were placed on open-file exhibit in Washington, D. C. and Amarillo, Texas. The purpose of the exhibit material was to assist private companies in reaching decisions regarding their participation in the Helium Conservation Program.

Because the information contained in the two reports on exhibit contain data for natural gases of higher helium and nitrogen concentrations than may be expected in those systems to be processed in the conservation program, it was decided to supplement the original exhibit material with experimental phase

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\* Press Release: May 1, 1958, Secretary of the Interior Seaton announces New National Policy to conserve Helium.

Press release: August 19, 1958, Department Proposes Legislation to Conserve Helium.







relationship data from a system more representative of the natural gases which will be processed in the conservation program.

The experimental data contained in this report were obtained from a helium-bearing natural gas considered typical of those to be processed in connection with the helium conservation program. Throughout this report this gas is identified as THC (Typical Helium Conservation) gas.

#### OBJECTIVES

The primary objective of this investigation was to obtain experimental phase relationship data at pressures from 100 to 500 p.s.i.a. and at temperatures ranging from -100 to -275° F., for a natural gas similar in composition to those systems likely to be processed in the proposed Helium Conservation Program. A determination of smoothed values of equilibrium vaporization coefficients for methane, ethane, nitrogen, and helium was also desired.

A secondary objective of this study was the determination of the effect of removing heavy hydrocarbons, in a preliminary trap, upon the phase behavior of the gas at 275 and 150 p.s.i.a. and at temperatures similar to those employed in the Bureau's present helium separation process.

#### SUMMARY AND CONCLUSIONS

A total of 158 samples of equilibrium vapor and liquid phases were obtained from 53 experimental conditions at 100, 150, 200, 275, 400, and 500 p.s.i.a. and at temperatures







from  $-100^{\circ}$  to  $-275^{\circ}$  F. One hundred six samples of equilibrium vapor and liquid phases were analyzed by means of a mass spectrometer. Fifty-two analyses for helium in the equilibrium liquid phases were made by means of a special apparatus which is superior to the mass spectrometer for measuring small concentrations of helium (1).

Vapor-liquid equilibria data for THC gas are presented in both tabular and graphic form. Percent-condensed calculations are also included, treating the gas as a four-component system composed of methane, ethane-plus, nitrogen, and helium.

Equilibrium vaporization coefficients,  $K_i$  (ratio of the mole fraction of a component in the vapor phase to its mole fraction in the liquid) were evaluated for methane, ethane, nitrogen, and helium, and are presented in tabular form. These data, except for helium and ethane, are shown graphically.

Solubility data for helium in the equilibrium liquid phases also were determined and are shown in Table II and Figure 6.

Results obtained when using a hydrocarbon trap may be summarized as follows:

1. A hydrocarbon trap eliminates the possibility of freezing occurring in the gas stream when it enters colder areas in the plant process. This avoids a serious operating difficulty.
2. The condensed hydrocarbons in the trap may be removed, separated, and preferentially disposed of for economic gain. Their removal imposes no significantly deleterious effect on the subsequent helium-extraction cycle.







3. The total amount of helium dissolved in the trap liquids should be small enough to be expendable.

4. No freeze-out of components occurred in this study with the hydrocarbon trap at 275 p.s.i.a. and  $-140^{\circ}$  F., regardless of whether natural gasolines had been previously removed.

5. The phase relationships existing in a gas-liquid separator are affected to some extent by the use of a hydrocarbon trap ahead of it. This is due to the fact that the feed gas to the trap and the feed gas to the separator have slightly different compositions. When a trap is employed, the concentration of methane in the liquid phase at the separator is higher than it would be if the trap were not used; conversely, the ethane-plus fraction in the liquid is reduced. The solubility of helium in the liquid at the separator is relatively constant, under a given set of conditions, regardless of whether a preliminary hydrocarbon trap is used.

6. The use of a preliminary hydrocarbon trap does not appear to complicate establishment of optimum conditions for operating a crude-helium separator. It should be pointed out that in selecting these conditions, the mole percent helium in the vapor phase is not the only criterion; the solubility of helium in the liquid phase is at least of equal importance.

#### ACKNOWLEDGMENT

The authors extend thanks to Will E. DeVaney for his conscientious attention to the details of operating the apparatus. He also arranged the tabular data and made the drawings for the report. Credit is also due William J. Boone, Jr., for his helpful suggestions during the course of this work.







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## I. Composition of a Typical Helium Conservation Gas

The helium-bearing natural gases found in the Texas and Oklahoma Panhandles, and in Southwestern Kansas, except for those supplying the Amarillo and Exell, Texas, and Keyes, Oklahoma, plants, may be considered as representative of the systems to be processed for helium when the Helium Conservation Program is implemented.

An experimental study of the phase relationships of one of these "typical" gases, referred to in this report as THC gas, has recently been completed and is the subject of this report.

Composition of the gas used in this experimental study is presented in Table 1, page 7. For convenience, the analysis is shown as 12- and 4-component system. Analysis for helium was by means of a special apparatus (1); all other components were determined by mass spectrometer (Consolidated Electrodynamics Corporation, Type 21-102, modified to Type 21-103).

## II. Determination of Phase Relationship Data

### A. Apparatus and Experimental Procedure

The apparatus used in this study was a U. S. Bureau of Mines Phase Equilibrium Apparatus, which has been described in the literature (2). Briefly, this apparatus consists of a windowed equilibrium cell which can be maintained at any desired temperature within the range from room temperature to  $-320^{\circ}$  F., and at any pressure to 4,000 p.s.i.a.







TABLE I

Percentage Composition of THC Gas (CO<sub>2</sub>- and H<sub>2</sub>O-free basis)

<u>Component</u>	<u>As 12-Component System</u>	<u>As 4-Component System</u>
Methane	71.7	71.7
Ethane	6.6	12.2
Propane	3.8	
n-Butane	.9	
i-Butane	.5	
n-Pentane	.1	
i-Pentane	.2	
Cyclopentane	Trace <sup>a</sup>	
Hexanes-plus	.1	
Nitrogen	15.2	15.3
Argon	.1	
Helium	.75 <sup>b</sup>	.75 <sup>b</sup>

<sup>a</sup> Less than 0.05 percent.<sup>b</sup> Special analysis. See Reference 1.







In the course of each experiment, THC gas was admitted to the apparatus and water and carbon dioxide were removed by contact with potassium hydroxide pellets in a trap. Pressure of the gas was then regulated to the desired value and the gas entered the windowed equilibrium cell maintained at the chosen temperature.

At the experimental conditions of temperature and pressure, partial condensation of the gas occurred, and by withdrawing the vapor phase at a slow rate, the quantity of liquid phase was allowed to increase. The cell contents were stirred vigorously to reach equilibrium conditions rapidly, and the mixture was then allowed to become quiescent and samples of both phases were withdrawn. Samples were analyzed by means of a mass spectrometer. An additional sample of each equilibrium liquid phase was taken for special analysis for helium by means of a Frost apparatus (1).

## B. Presentation and Discussion of Data

### 1. Vapor-liquid equilibria data

Results of mass spectrometer analyses of 58 samples of equilibrium vapor and liquid phases at 100, 200, 400 and 500 p.s.i.a. for temperatures between -100 and -275° F. are shown in Table II, pages 9 and 10. Values indicated for helium in the liquid phases were obtained by means of the special (Frost) apparatus.

The data contained in Table II were used in plotting Figures 1 - 4, pages 11 - 14. In these figures, data for helium solubility in liquids are not included; this is specially handled in a later section of this report.







TABLE II  
EQUILIBRIUM PHASE RELATIONSHIPS OF THC GAS - EXPERIMENTAL DATA

		100 p.s.i.a.			200 p.s.i.a.			400 p.s.i.a.			500 p.s.i.a.		
		V <sup>a</sup>	L <sup>b</sup>	K <sup>c</sup>	V	L	K	V	L	K	V	L	K
-100°F.	Methane	74.9	9.4	7.97	76.4	18.4	4.152	77.2	35.5	2.175	77.1	44.0	1.752
	Ethane	6.1	18.1	0.337	4.8	23.1	0.208	3.6	29.7	0.121	3.3	22.9	0.144
	Ethane-Plus	8.1	90.5	0.0895	5.8	81.4	0.0712	4.2	64.3	0.0653	3.8	54.7	0.0695
	Nitrogen	16.1	0.1 <sup>d</sup>	-	17.0	0.1 <sup>d</sup>	-	17.7	0.0	-	18.1	1.4	12.9
	Helium	0.8	0.001 <sup>d</sup>	-	0.9	0.007	130	0.9	0.008	110	1.0	0.011	90.9
-125°F.	Methane	76.3	12.0	6.358	77.7	24.7	3.146	78.1	53.7	1.454	76.0	59.8	1.271
	Ethane	4.9	24.7	0.198	3.5	29.4	0.119	2.2	23.6	0.0932	1.8	18.8	0.0957
	Ethane-Plus	6.0	87.9	0.0683	3.8	75.3	0.0505	2.4	45.0	0.0533	2.0	37.5	0.0533
	Nitrogen	17.0	0.1 <sup>d</sup>	-	17.6	0.1 <sup>d</sup>	-	18.7	1.1	17.0	20.9	2.8	7.46
	Helium	0.8	0.001 <sup>d</sup>	-	0.9	0.002 <sup>d</sup>	-	0.8	0.008	100	1.1	0.016	68.7
-150°F.	Methane	78.5	19.1	4.110	78.6	42.6	1.845	72.1	64.9	1.111	66.2	68.4	0.9678
	Ethane	3.0	34.3	0.0874	1.8	30.6	0.0588	0.9	15.7	0.057	0.8	11.1	0.072
	Ethane-Plus	3.2	80.8	0.0396	1.9	57.0	0.0333	1.0	31.6	0.0316	0.9	24.9	0.036
	Nitrogen	17.5	0.0	-	18.6	0.2	93	25.5	3.6	7.08	30.6	6.9	4.43
	Helium	0.8	0.001 <sup>d</sup>	-	0.9	0.002 <sup>d</sup>	-	1.4	0.018	77.8	2.3	0.060	38.3
-175°F.	Methane	79.2	29.9	2.649	74.8	64.1	1.167	52.8	74.8	0.7059	46.3	71.6	0.6466
	Ethane	1.3	34.2	0.0380	0.5	17.7	0.028	0.4	7.7	0.052	0.3	7.2	0.042
	Ethane-Plus	1.4	70.0	0.0200	0.5	34.6	0.014	0.5	14.3	0.035	0.3	15.2	0.020
	Nitrogen	18.5	0.0	-	23.5	1.3	18.1	41.7	10.9	3.826	42.9	13.1	3.275
	Helium	0.9	0.002 <sup>d</sup>	-	1.1	0.004 <sup>d</sup>	-	5.1	0.068	75.0	10.4	0.185	56.22

a - Mole percent composition, Vapor phase

b - Mole percent composition, Liquid phase

c - Equilibrium vaporization coefficient, V/L

d - These values are of questionable accuracy.







TABLE II (Continued)  
EQUILIBRIUM PHASE RELATIONSHIPS OF THE GAS - EXPERIMENTAL DATA

		100 p.s.i.a.			200 p.s.i.a.			400 p.s.i.a.			500 p.s.i.a.		
		V	L	K	V	L	K	V	L	K	V	L	K
-200° F.	Methane	77.5	60.9	1.272	55.0	73.2	0.7514	33.5	73.1	0.4583	14.1	72.7	0.1939
	Ethane	0.4	21.1	0.019	0.2	11.2	0.018	0.3	6.8	0.044	0.1	6.6	0.15
	Ethane-Plus	0.4	38.8	0.010	0.2	21.3	0.0094	0.7	12.1	0.058	0.2	11.8	0.017
	Nitrogen	21.0	0.4	52	41.7	5.6	7.45	45.3	14.9	3.040	38.6	15.3	2.523
	Helium	1.1	0.002 <sup>d</sup>	-	3.2	0.011	291	20.5	0.191	107.3	47.3	0.352	134.4
-225° F.	Methane	52.1	77.4	0.6731	31.6	69.0	0.4580	17.1	73.2	0.2336	9.6	71.6	0.134
	Ethane	0.1	9.0	0.011	0.2	8.9	0.023	0.1	6.8	0.015	0.1	6.5	0.015
	Ethane-Plus	0.2	17.9	0.011	0.4	18.9	0.021	0.3	11.7	0.026	0.1	11.2	0.0089
	Nitrogen	45.0	4.6	9.78	52.4	12.1	4.331	33.3	14.8	2.250	27.8	16.7	1.665
	Helium	2.7	0.010	270	15.7	0.040	393	49.4	0.198	249.5	62.6	0.329	190.3
-250° F.	Methane	24.7	73.4	0.3365	14.7	70.5	0.2085	8.4	72.4	0.116	6.0	72.1	0.0832
	Ethane	0.1	8.1	0.012	0.3	7.1	0.042	0.1	6.7	0.015	0.0	6.6	-
	Ethane-Plus	0.1	16.4	0.0061	0.5	14.7	0.034	0.2	11.5	0.017	0.0	11.5	-
	Nitrogen	66.0	10.0	6.600	42.6	14.9	2.859	22.0	15.8	1.392	17.5	16.1	1.087
	Helium	9.3	0.008	1200	41.6	0.062	671	69.4	0.158	439.2	76.5	0.215	355.8
-275° F.	Methane	9.7	70.5	0.138									
	Ethane	0.1	7.5	0.013									
	Ethane-Plus	0.1	16.3	0.0061									
	Nitrogen	46.5	13.2	3.523									
	Helium	43.8	0.030	1460									



1871 1872 1873

1874 1875 1876

1877 1878 1879

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1880 1881 1882

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1895 1896 1897

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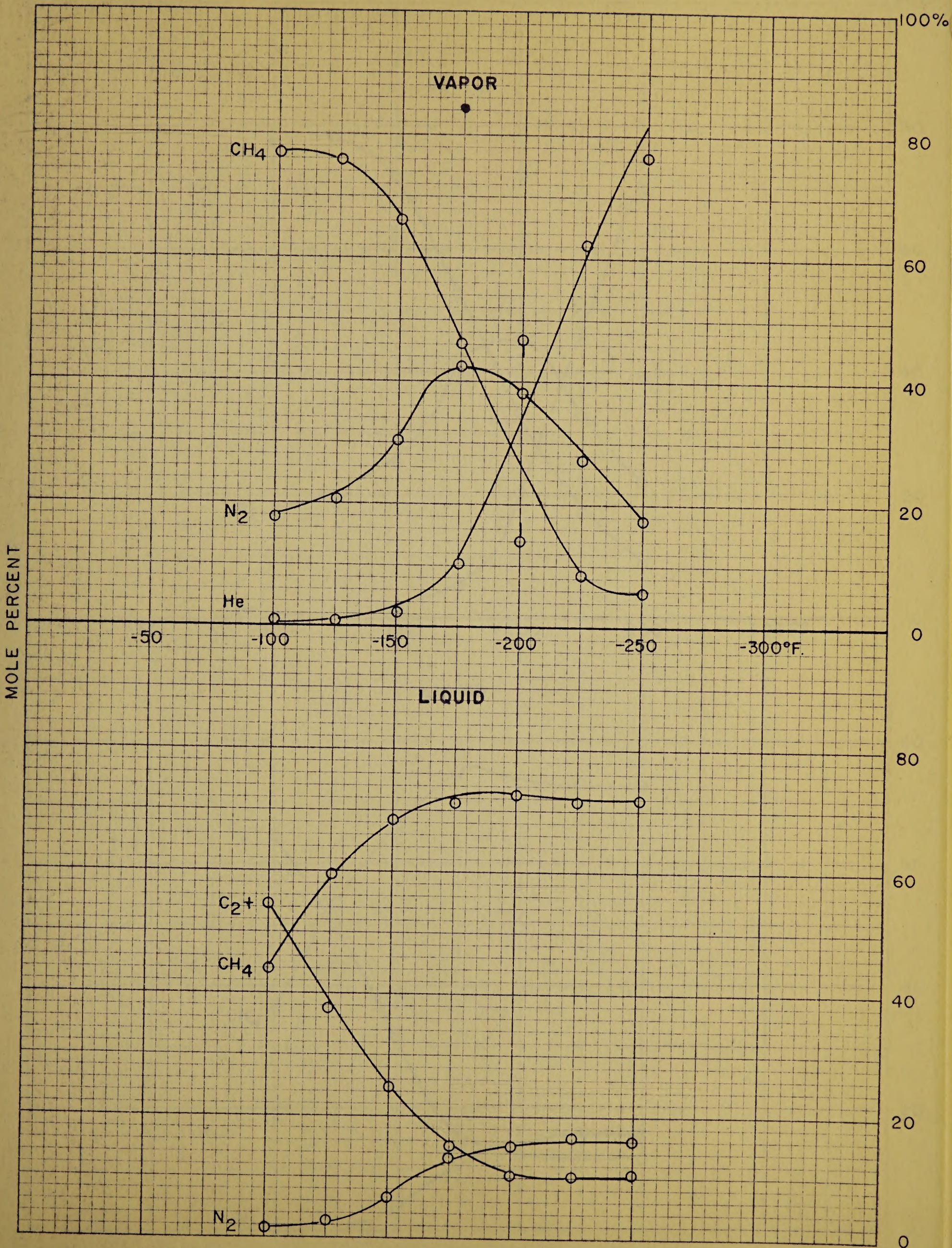
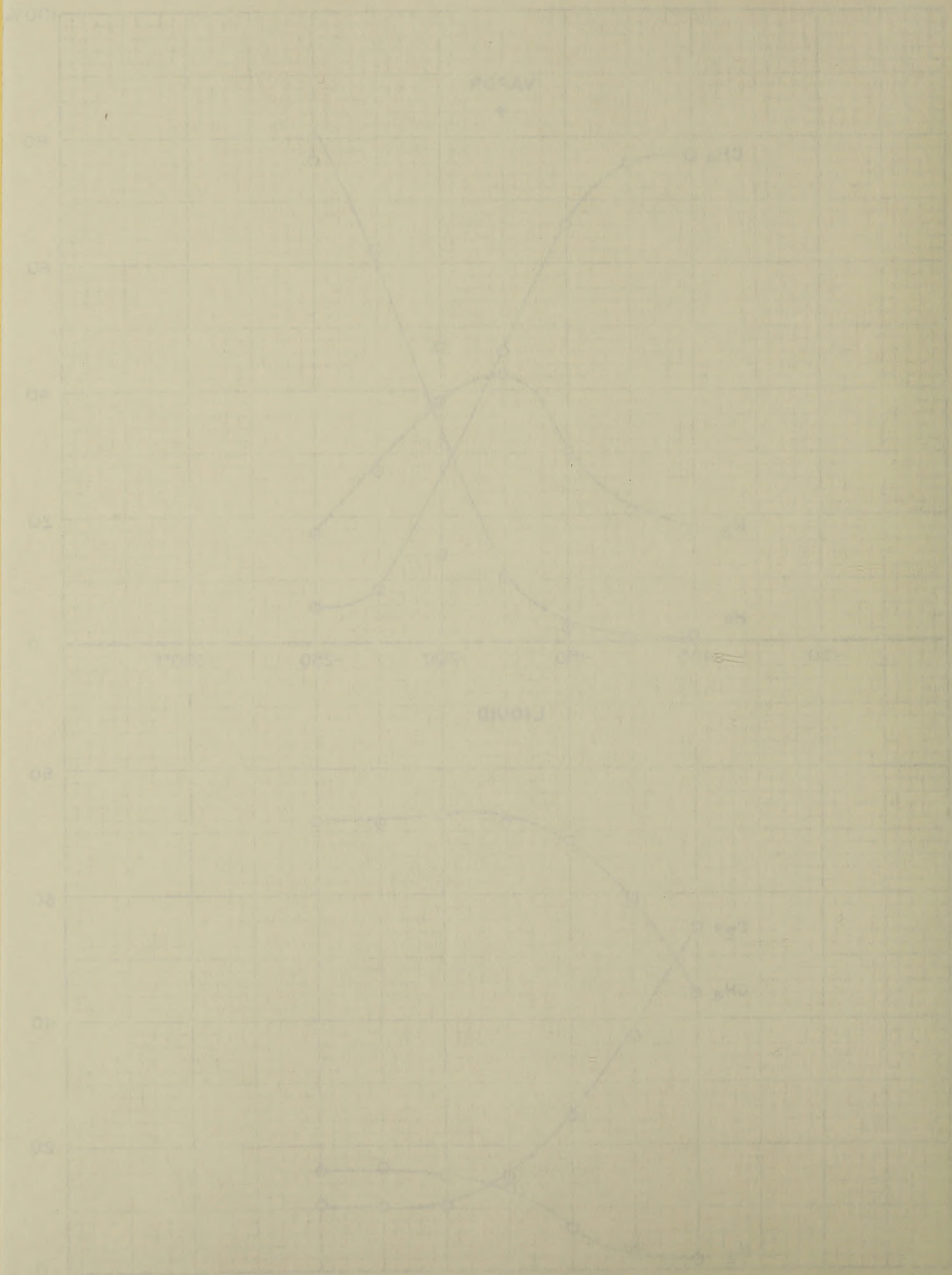


FIGURE 1. PHASE RELATIONSHIP DATA, THC GAS, 500 p.s.i.a.





TEMPERATURE

FIGURE 1. PHASE BEHAVIOR DATA, THE GAS, 500-600°K.



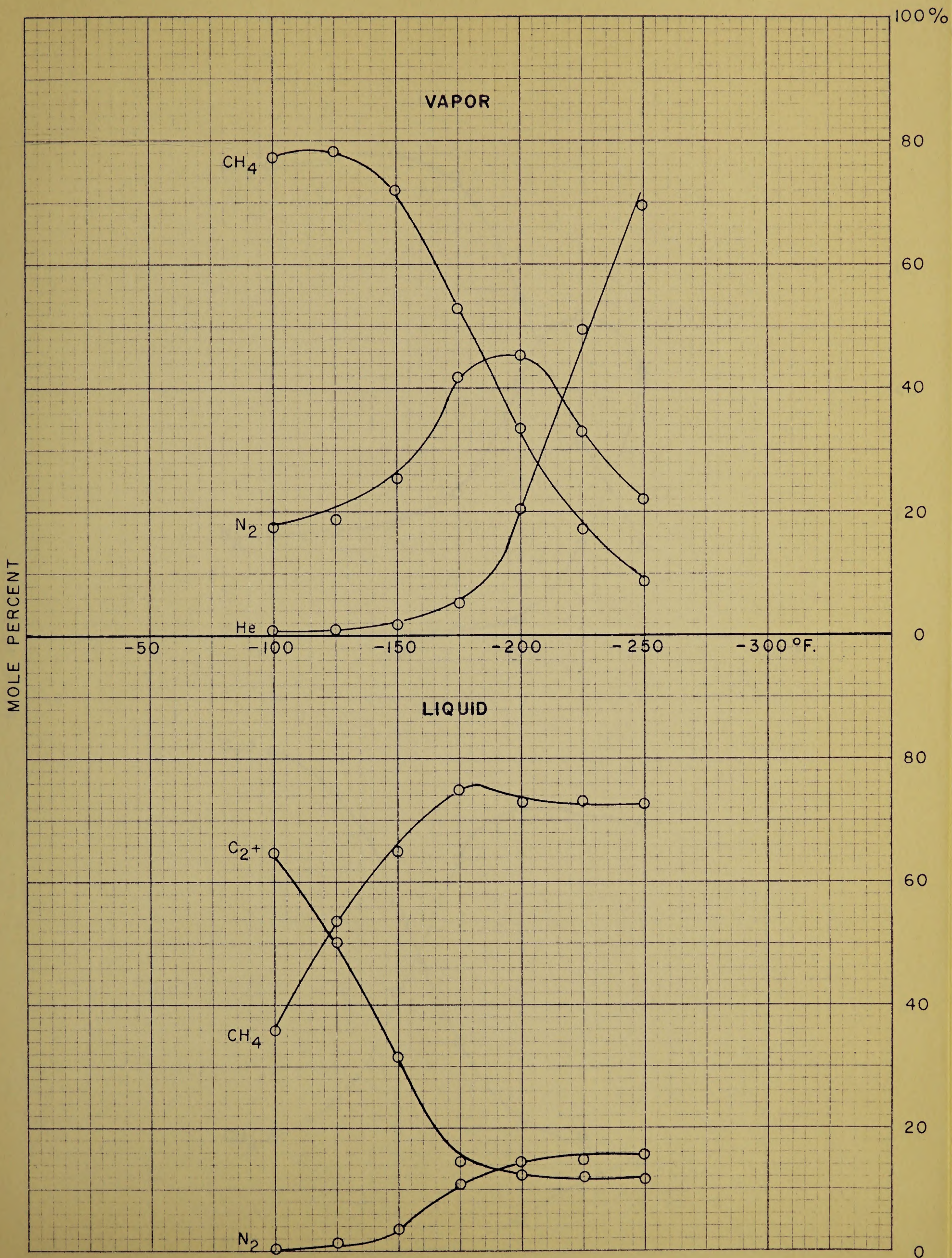
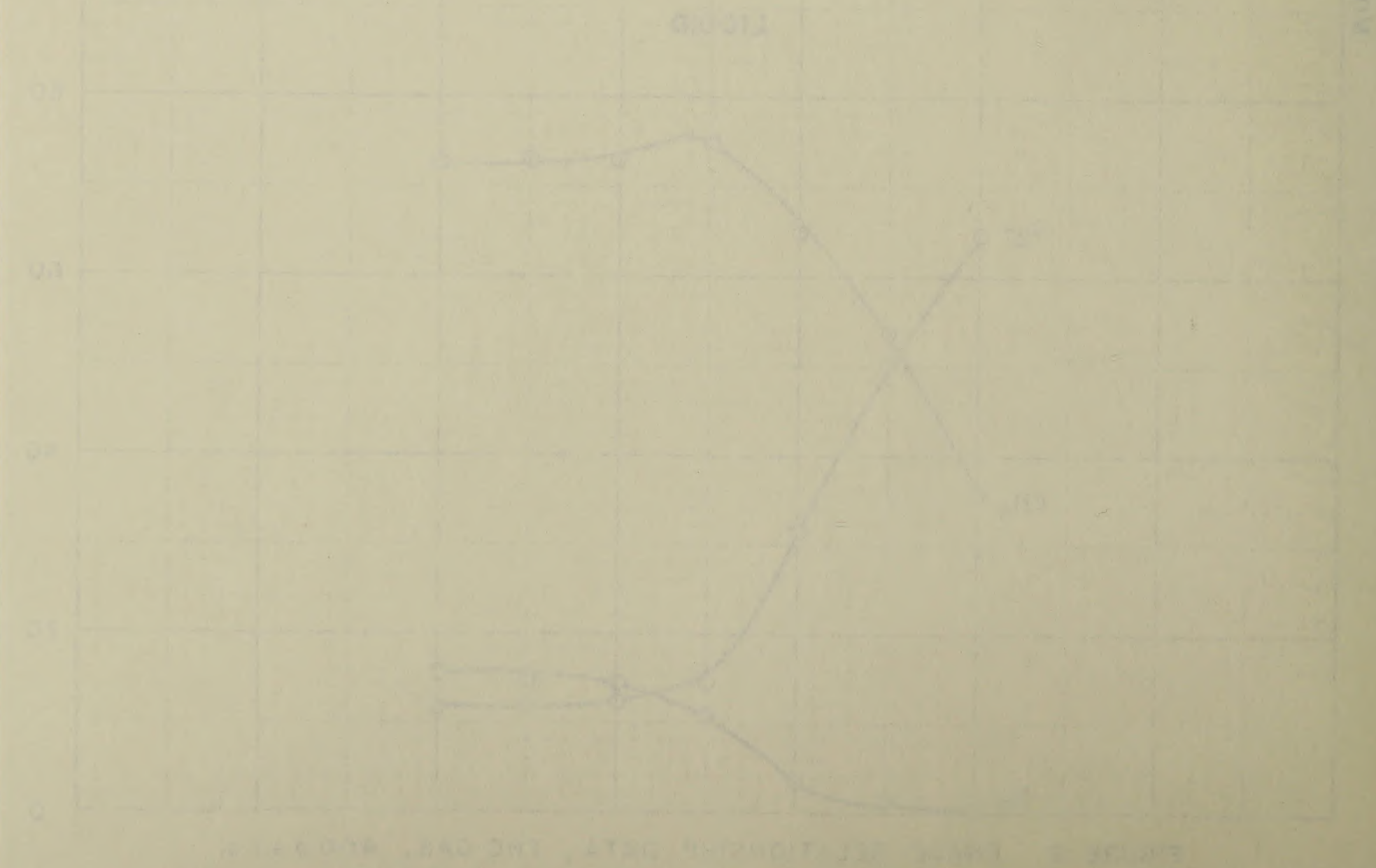
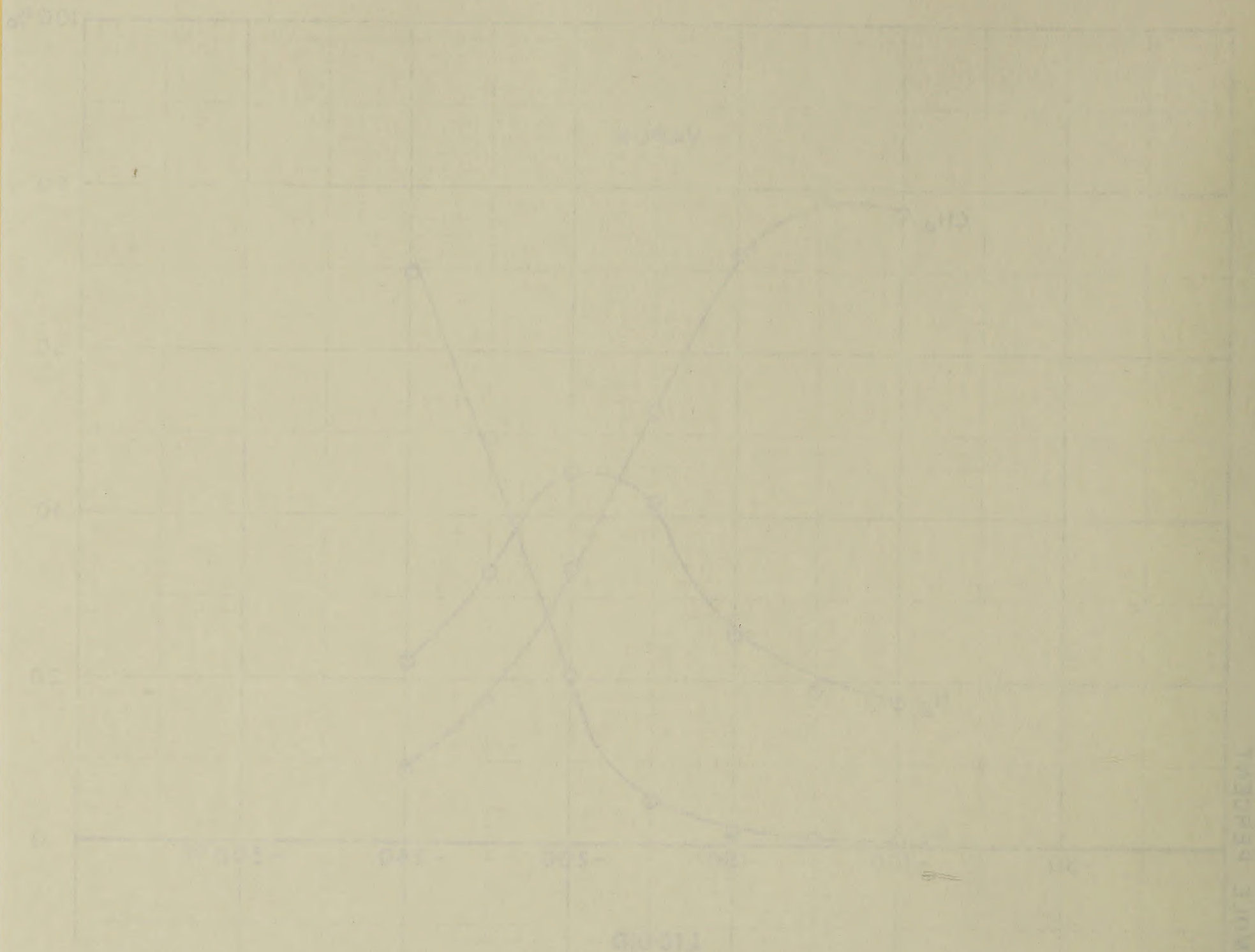


FIGURE 2. PHASE RELATIONSHIP DATA, THC GAS, 400 p.s.i.a.







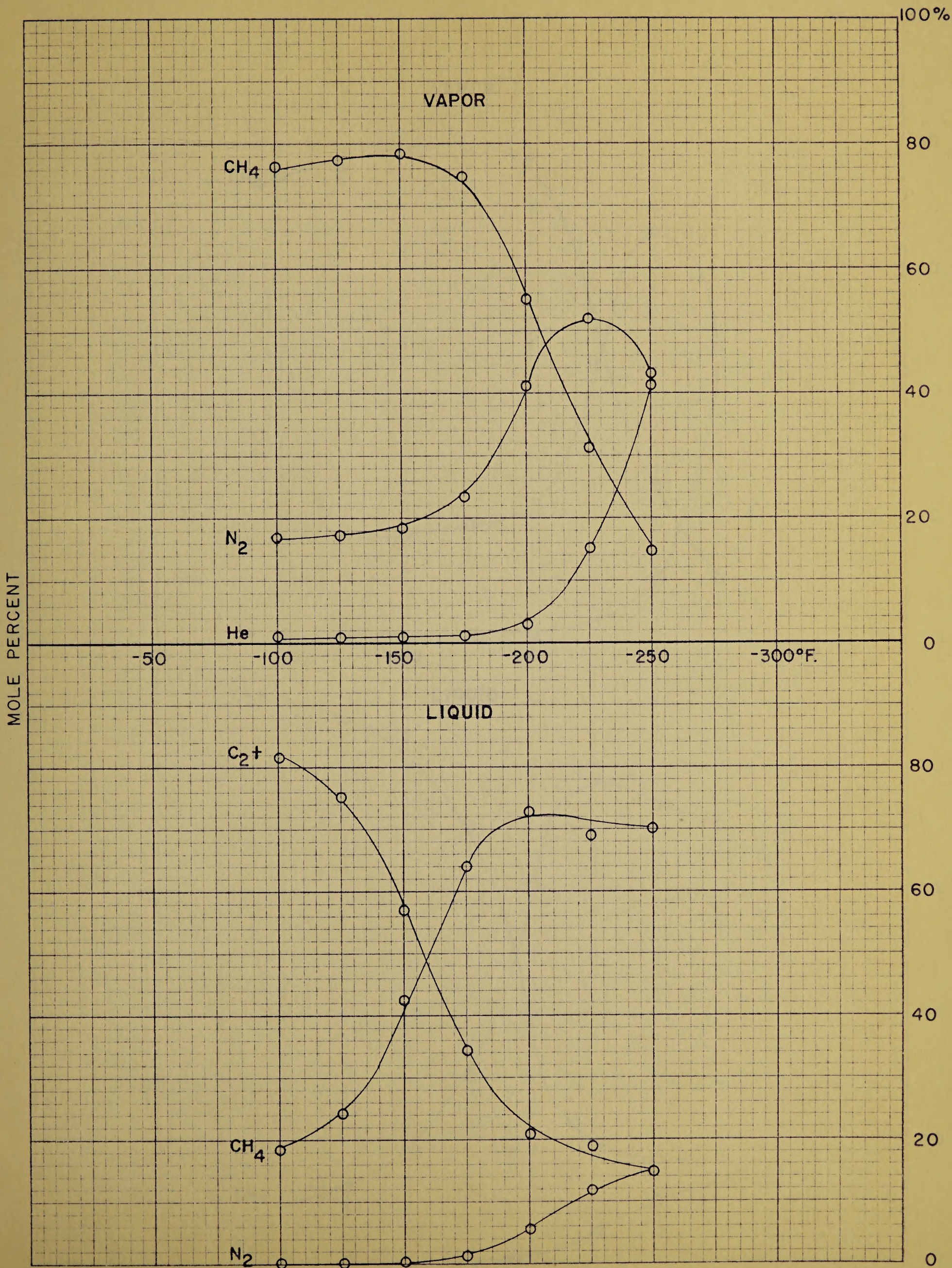
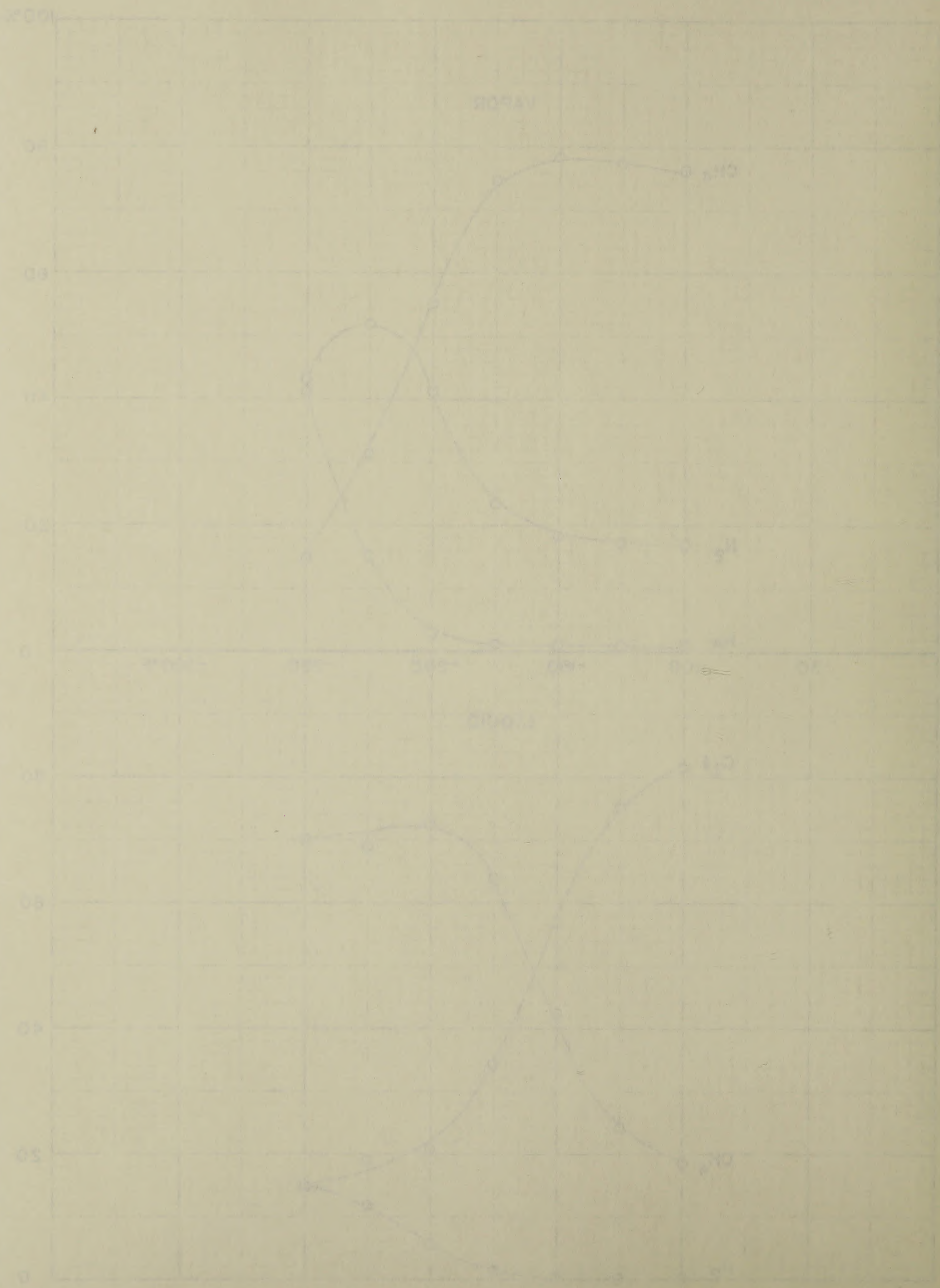


FIGURE 3. PHASE RELATIONSHIP DATA, THC GAS, 200 p.s.i.a.





NOTE: VAPOR



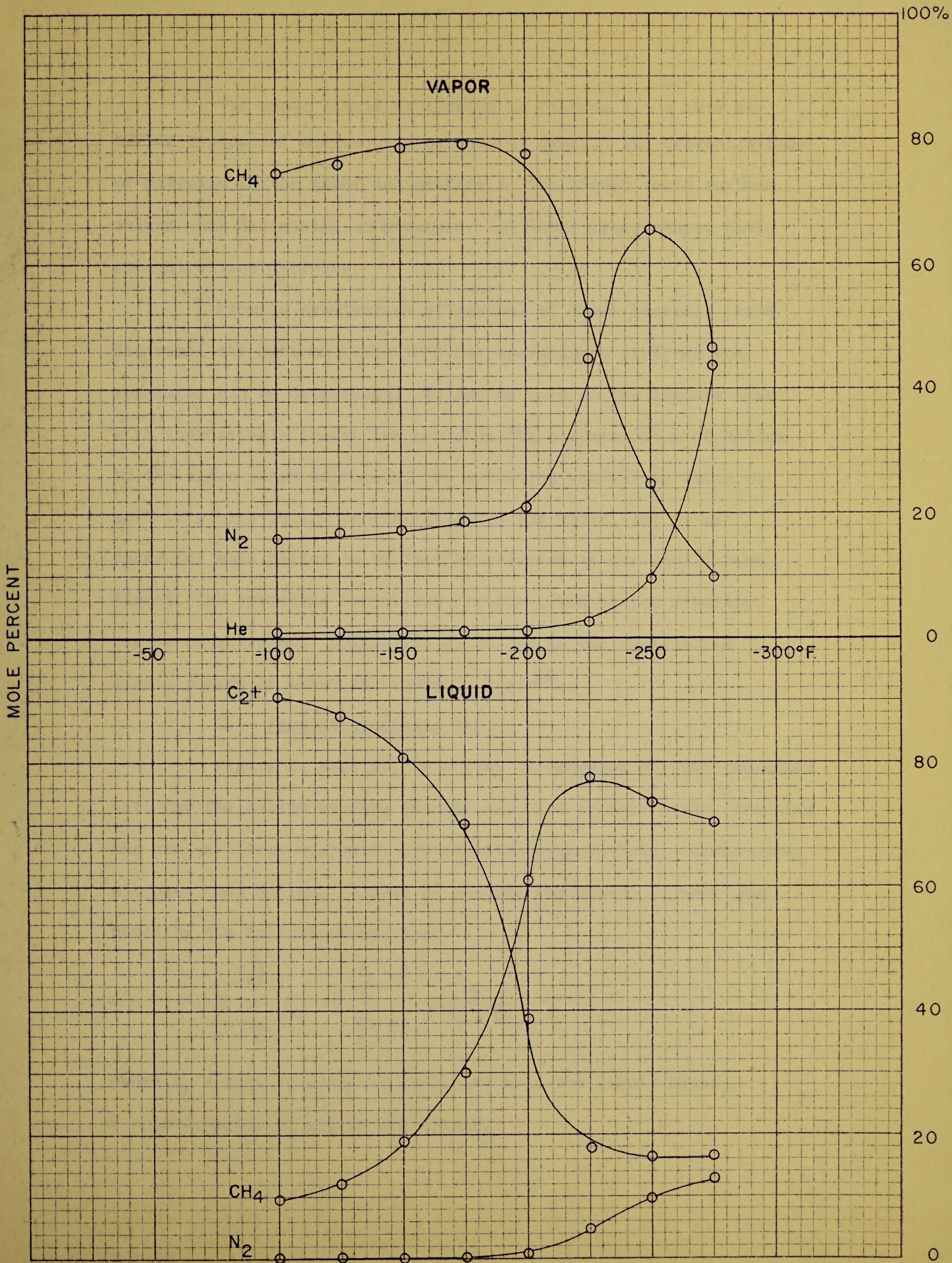
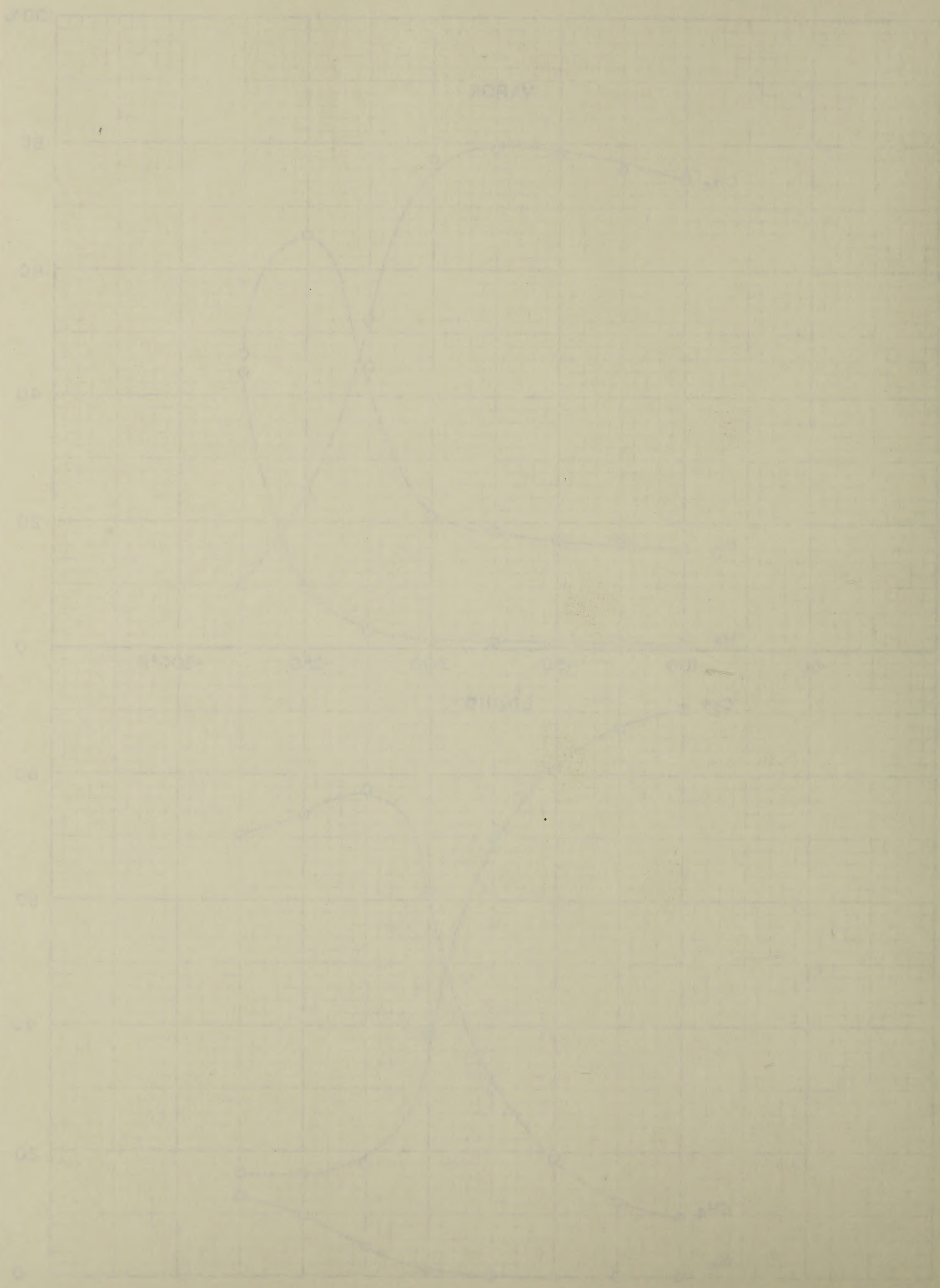


FIGURE 4. PHASE RELATIONSHIP DATA, THC GAS, 100 p.s.i.a.







The vapor-liquid data shown in Figures 1 - 4 show behavior typical of helium-bearing natural gases. The concentrations of nitrogen in the vapor and methane in the liquid reach maximum values with decreasing temperature. At lower temperatures these concentrations decrease.

From an examination of several of these isobaric phase diagrams, the optimum conditions for operating a crude-helium separator can be determined. It can be seen in the figures that with increasingly colder temperatures the concentration of helium in the vapor phase increases. By selecting conditions which result in a high helium concentration in the vapor, yet do not cause too much helium to be lost by solution in the equilibrium liquid, the operating conditions for the crude-helium separator can be established. Solubility of helium in the equilibrium liquid phases is shown in Figure 6, page 19.

## 2. Percent condensed data

Figure 5, page 16, is a plot of computed percent-condensed data for the helium-bearing natural gas used in this study, treating the gas as a four-component system containing methane, ethane-plus, nitrogen, and helium. Values of percent-condensed,  $L$ , were computed by the following equation:

$$\sum_{k=1}^{k=j} x_k = \sum_{k=1}^{k=j} \frac{F n_k}{L + V K_k} = 1$$

where  $x_k$  = mole fraction of component  $k$  in the liquid phase,

$F$  = total moles of gas in the system,



The report of the committee on the subject of the  
proposed amendment to the constitution of the  
association is hereby submitted to the association  
for their consideration. The committee has  
the honor to acknowledge the receipt of the  
report of the committee on the subject of the  
proposed amendment to the constitution of the  
association, and to express its appreciation of the  
care and attention which the committee has  
devoted to the study of the subject. The  
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PERCENT CONDENSED

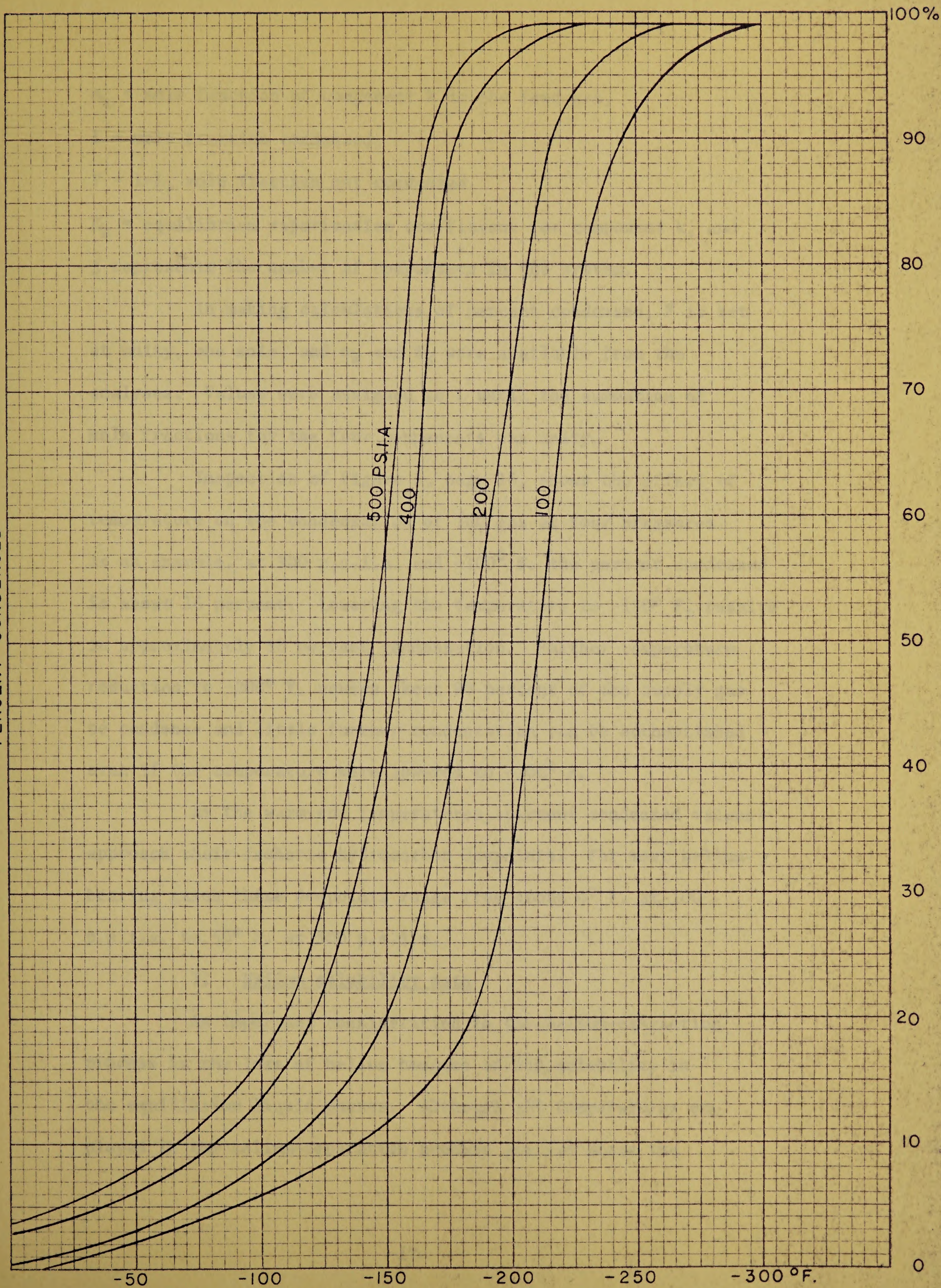


FIGURE 5. ISOBARIC PERCENT CONDENSED DATA, THC GAS



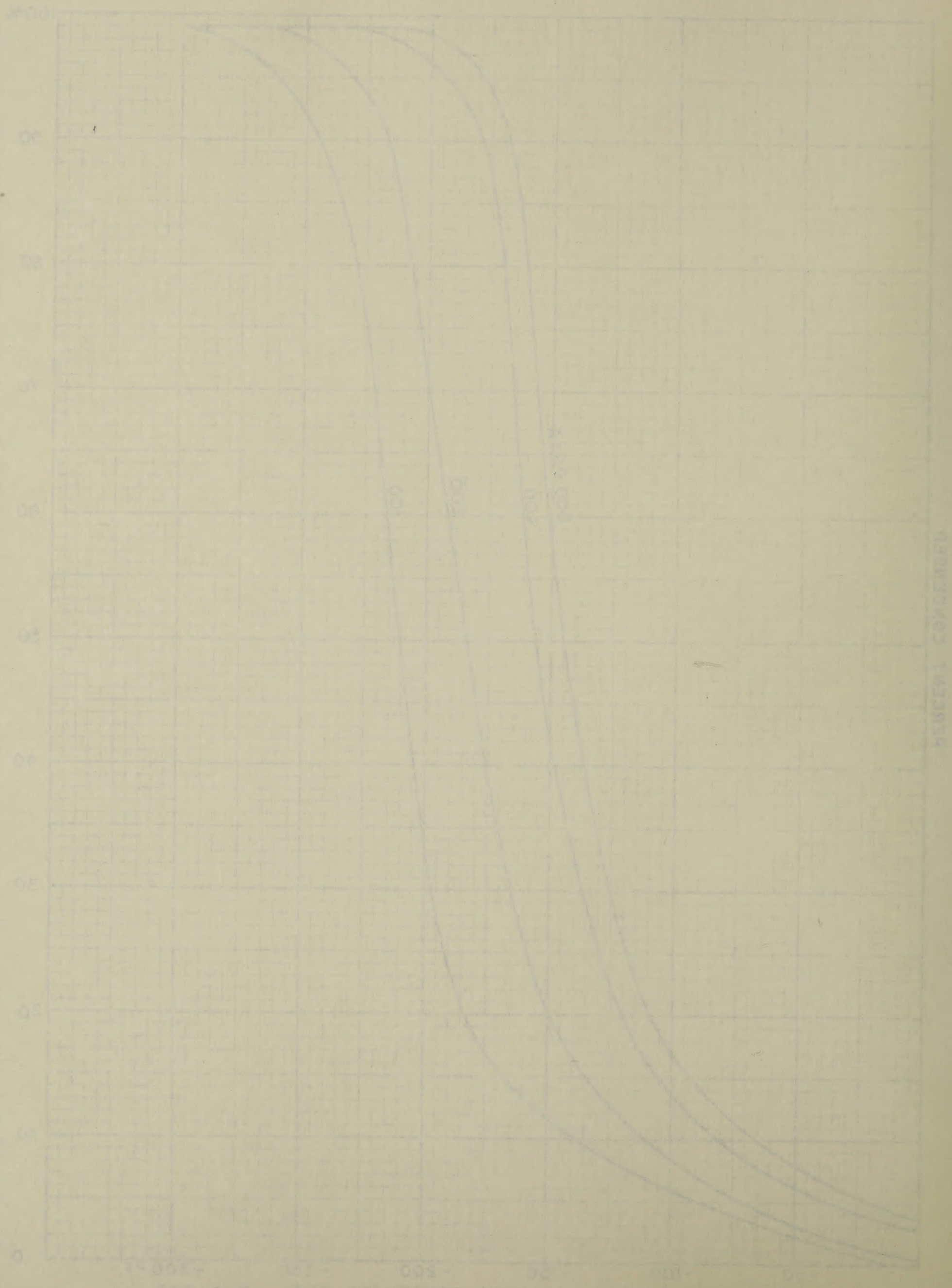


FIGURE 2. ISOBARIC VAPOR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM

PERCENT CONDENSED



$n_k$  = mole fraction of component k in the feed gas,

$L$  = mole fraction condensed,

$V = 1-L$ , mole fraction not condensed,

$K_k$  = equilibrium vaporization coefficient for component k, and  
j represents the number of components in the system.

In making calculations of percent condensed, F is set at unity, one mole, and  $n_k$  and  $K_k$  were available from the analyses. Values were assigned to L until the summation of mole fractions for the four components was unity.

Inspection of Figure 5, page 16, shows the effect of temperature on the condensation of THC gas at four pressures. As an example, at 500 p.s.i.a. and  $-100^{\circ}$  F. the percent condensed is about 16 percent. Lowering the temperature to  $-150^{\circ}$  F. results in approximately 56 percent condensation. Further temperature reduction to  $-200^{\circ}$  F. causes about 98 percent of the supply gas to condense and little further condensation can be accomplished even if the temperature were lowered to  $-300^{\circ}$  F.

At the warm-end temperatures, percent condensed values approach their isobaric hydrocarbon dewpoints. For most helium-bearing gases these dewpoints range from about  $0^{\circ}$  F. at 100 p.s.i.a. to  $50^{\circ}$  F. at 500 p.s.i.a.

### 3. Helium solubility data

An important consideration in the helium-extraction process is the loss of helium because of its solubility in the equilibrium liquid phases. Although all temperatures employed in the helium-separation process are far above the







critical temperature of helium ( $-450.2^{\circ}$  F.), small concentrations of this component are always present in the liquids. The solubility of helium is, therefore, an important consideration when computing the separation efficiency of a plant process.

The mole percent helium in the equilibrium liquid phase for each experimental condition is shown in Table II, pages 9 and 10. These values were obtained by special analysis with a Frost apparatus (1). Smoothed plots of these data are shown in Figure 6, page 19. Values less than 0.005 percent are subject to considerable inaccuracy.

Although Table II, pages 9 and 10, contains data for the solubility of helium in the equilibrium liquid phase for each experimental condition, not all the tabular values were utilized in preparing the smooth curves shown in Figure 6. Values less than 0.005 percent helium (marked by an asterisk in Table II) are of questionable accuracy because of limitations in reproducibility in obtaining and analyzing samples containing low concentrations ( $<0.005$  percent) of helium.

Regardless of the recognized limitations of accuracy in the data, the curves shown in Figure 6 are considered reasonably representative for the solution of helium in the equilibrium liquid phases. The trend of solution characteristics for helium is now being investigated at this laboratory. Several natural gases have already been studied. A comparison of Figure 6 with data from the other systems indicates conformity to usual solution behavior of helium in the equilibrium liquid phases.



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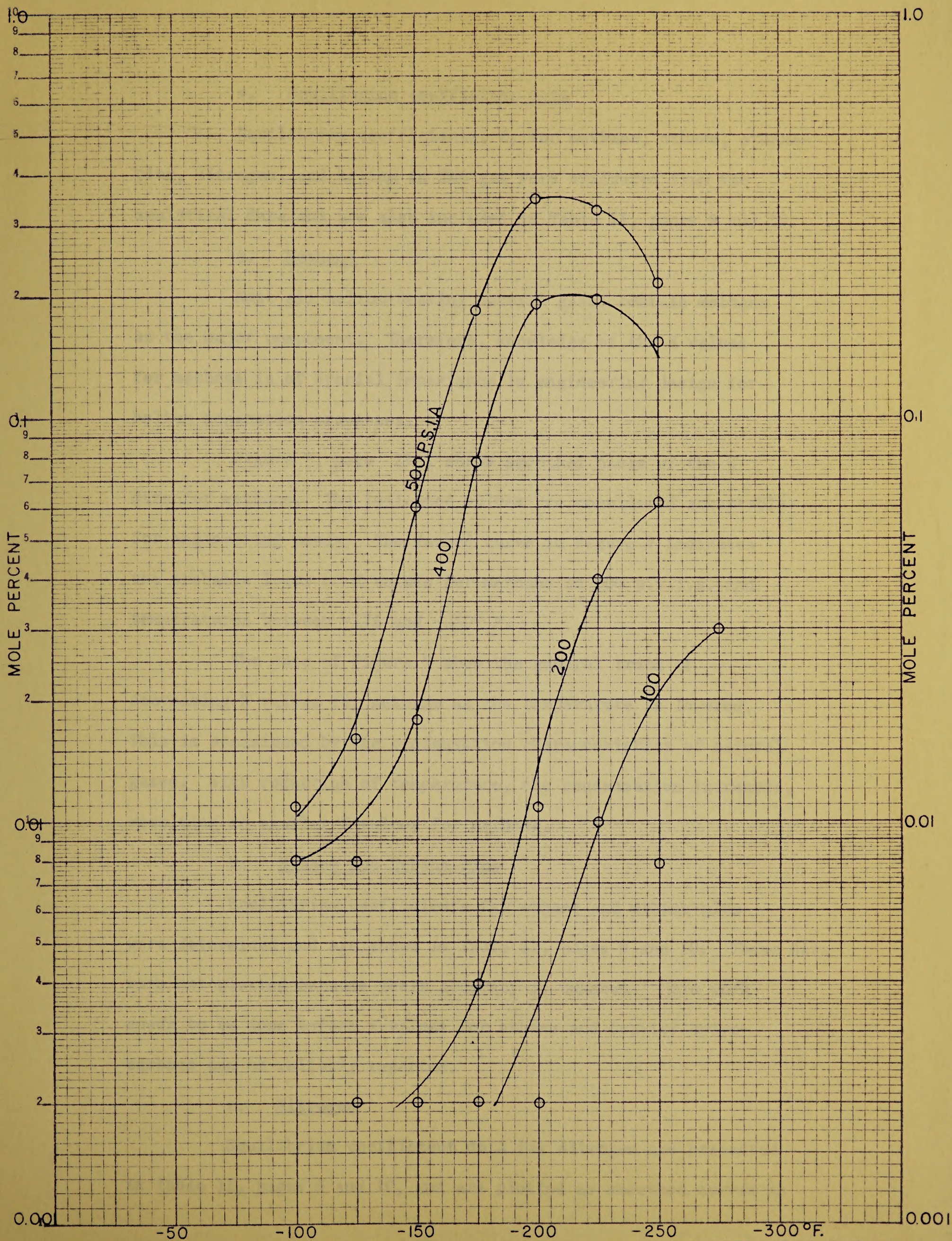


FIGURE 6. SOLUBILITY OF HELIUM IN EQUILIBRIUM LIQUID PHASES, THC GAS



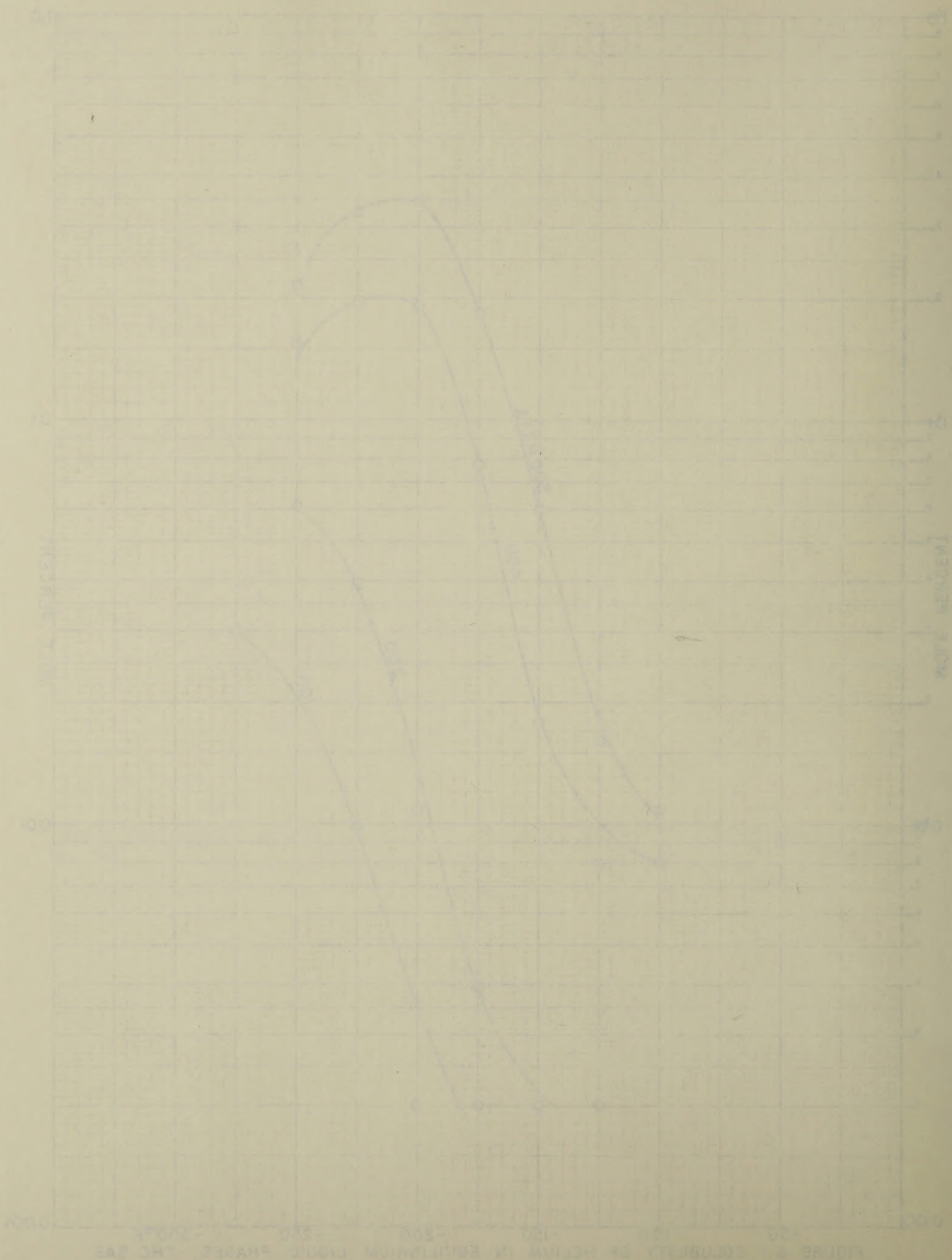


FIGURE 2. SOLUBILITY OF HELIUM IN EQUILIBRIUM LIQUID PHASE. THE GAS



#### 4. Equilibrium coefficient data

Equilibrium coefficients, K, for methane, ethane, ethane-plus, nitrogen, and helium in THC gas were evaluated from the analytical data and are also included in Table II, pages 9 and 10.

##### a. Methane

Most all helium-bearing natural gases contain methane as the major component. Therefore, knowledge of the K values for methane is of special importance in engineering design for helium separation processes.

Figure 7, page 21, shows smoothed plots of the K data for methane. The indicated values are considered acceptable for engineering needs. The dashed curve in Figure 7 indicates the probable locus of K values for methane at 500 p.s.i.a. and temperatures between -175 and -250° F.

The data of Figure 7 show the general trend of decreasing K values for methane as the temperature is lowered. This is occasioned by the condensation characteristics of natural gases. With reduction of temperature, the condensation increases, resulting in smaller K values for methane.

##### b. Ethane and Ethane-Plus

Equilibrium coefficients for ethane and ethane-plus were determined and are shown in Table II, pages 9 and 10. These data were not plotted because their accuracy is unknown. More work needs to be done before K values for ethane and heavier hydrocarbons can be reliably reported.

##### c. Nitrogen

Equilibrium coefficient data for nitrogen are presented in Table II, pages 9 and 10, and are plotted as smoothed curves in







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2 CYCLES X 70 DIVISIONS

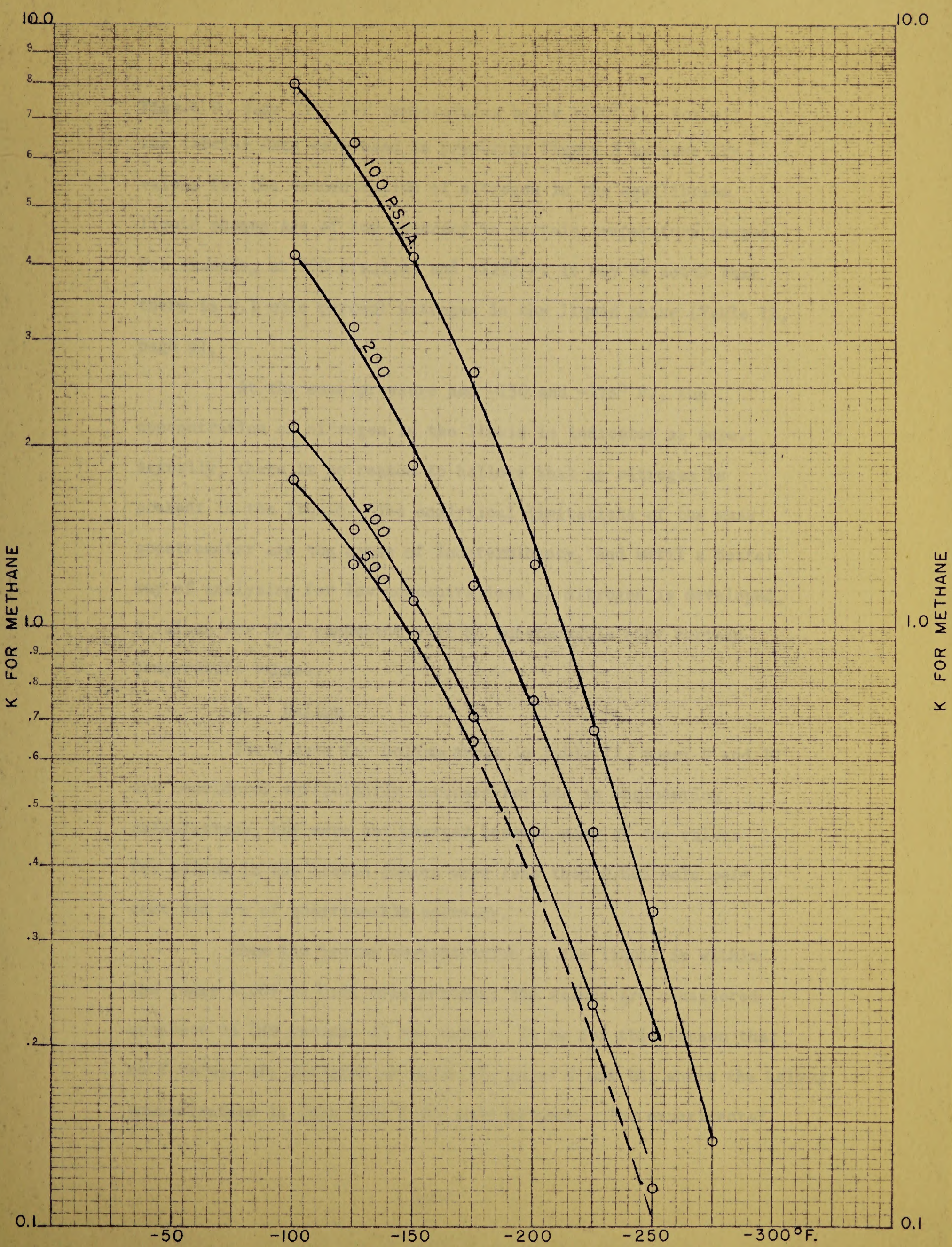


FIGURE 7. EQUILIBRIUM COEFFICIENTS FOR METHANE, THC GAS



EMPIRICAL

20

20

0.1

0.1

FIGURE 1. EQUILIBRIUM COEFFICIENTS FOR METHANE IN THE GAS

EMPIRICAL

EMPIRICAL





Figure 8, page 23 , for temperatures below  $-100^{\circ}$  F. Not all the tabular data were used in preparing Figure 8 because the values for the concentration of nitrogen in the equilibrium liquid phases are of low accuracy in certain temperature ranges. For example, at 100 p.s.i.a. and  $-125^{\circ}$  F. it may be noted that there is 0.1 mole percent nitrogen in the liquid phase (Table II, page 9).

At the same pressure and  $-150$  and  $-175^{\circ}$  F., the concentration of nitrogen in the liquid is indicated as zero. Actually, there is no reason to believe that no nitrogen is present in the liquid. The analytical limitations of the mass spectrometer are the cause of indeterminacy, and until a better way of analyzing for low concentrations of nitrogen is developed, K values for this component will be questionable over certain temperature ranges.

d. Helium

The K data for helium, shown in Table II, pages 9 and 10 are considered sufficiently accurate for use in engineering calculations, but were not plotted because many of the values for helium in the liquid phases were less than 0.005 mole percent and are of questionable accuracy.

When the helium concentration in the liquid is within the range 0.005 to 0.01 mole percent, the values are considered accurate to  $\pm 40$  percent of the value. It is for this reason that no K values are included in Table II, pages 9 and 10, where the helium concentration is less than 0.005 mole percent. The experimental



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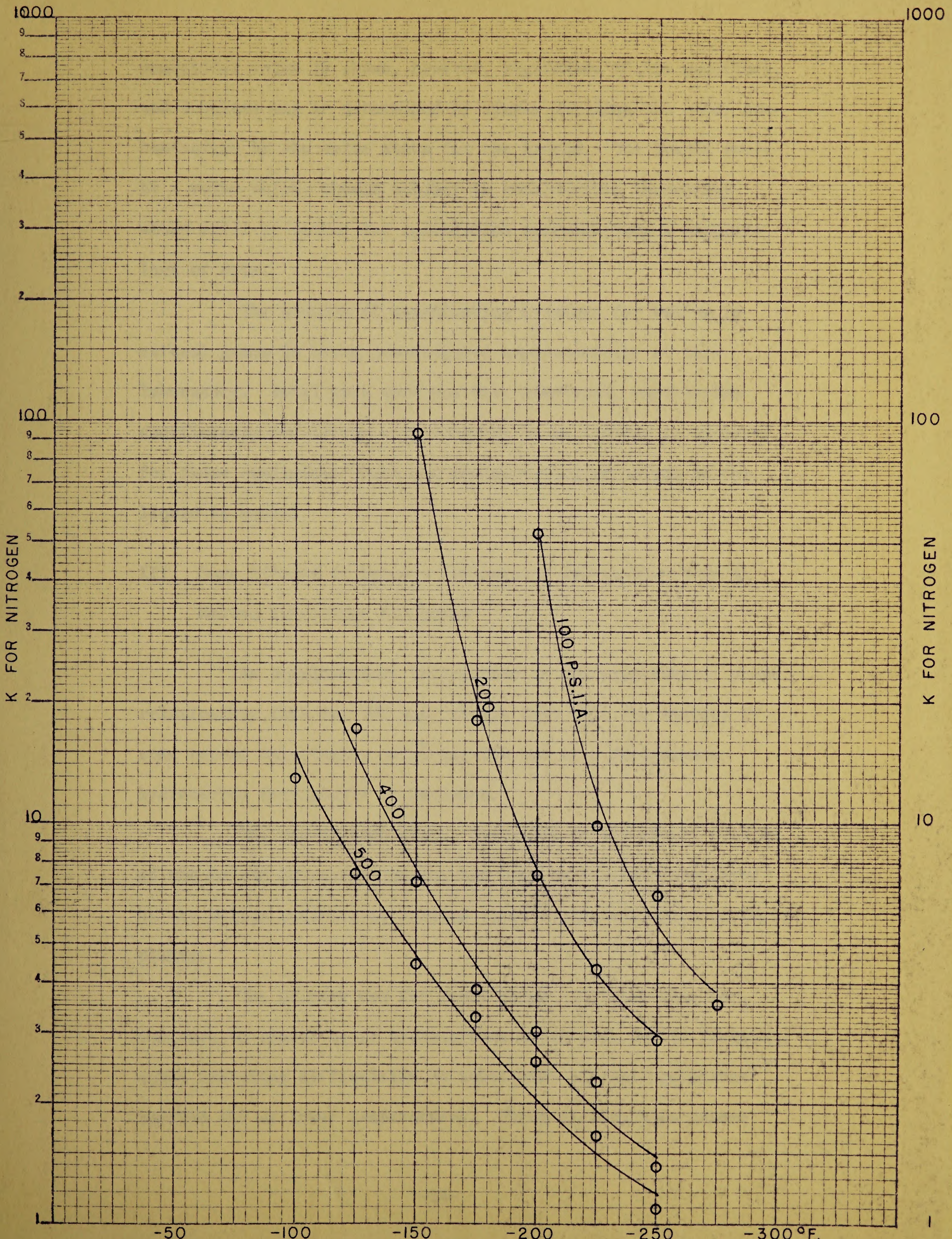


FIGURE 8. EQUILIBRIUM COEFFICIENTS FOR NITROGEN, THC GAS



100

100

100

100

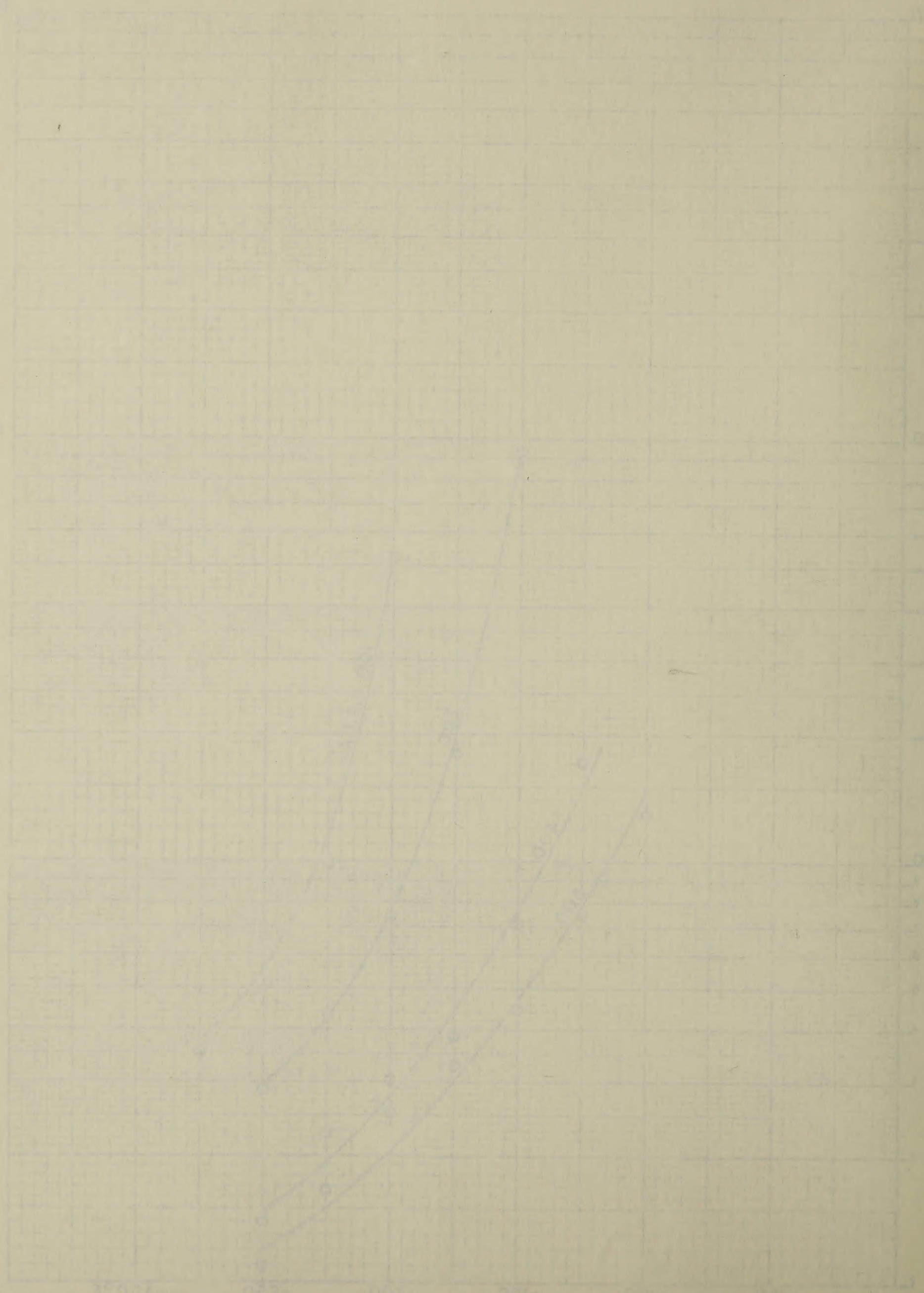
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FIGURE 8. EQUILIBRIUM COEFFICIENTS FOR NITROGEN AND CARBON





analytical value is shown, however, regardless of its magnitude, and K values may be determined by simply dividing the vapor concentration by the value shown for the liquid. The result would be a value which, though subject to considerable inaccuracy, would still be better for calculation purposes than a complete lack of data.

The problem of establishing K values for helium in natural gases is being investigated experimentally at this laboratory. Until more work has been completed, equilibrium coefficients for helium will continue to be limited in accuracy for those conditions where the concentration of helium in the liquid is small.

### III. Some Effects of Using a Preliminary Hydrocarbon Trap in Helium Extraction Processes

As supplementary information to the experimental phase relationship data for THC gas, it was felt that the results of some recent experiments involving the use of a preliminary hydrocarbon trap should be included.

The use of such traps, installed in the warmer portion of the helium extraction cycle, has been successfully employed by the Helium Activity at various times in the operation of their plants.

The primary use for these traps, at least thus far, has been to remove heavy hydrocarbons which may, due to freezing, cause operating difficulties in subsequent process operations carried out at lower temperatures. These difficulties assume







many forms, such as liquid-level controllers and indicators giving spurious indications, loss of valve control over throttling, and even complete restriction of gas flow. The troubles occasioned by the freezing of heavy hydrocarbons may even result in shutdown of the plant until the hydrocarbons can be thawed and removed.

For a schematic flow diagram of the helium process cycle, the reader is referred to the Preface of "Open File of Information and Data Relating to the Extraction of Helium from Natural Gas By Low-Temperature Processes," dated May 1, 1959. Copies of this report are available at the Helium Liaison Office, Washington, D. C., and at the office of the Assistant Director--Helium, Amarillo, Texas.

As a part of this investigation it was desired to conduct limited experiments to point out some of the uses of hydrocarbon traps. For these experiments, THC gas of the composition shown in Table I, page 7, was used. This gas, at 275 p.s.i.a., was subjected to temperatures of -80, -100, -120, and -140° F. to simulate operating conditions for a hydrocarbon trap. Equilibrium vapor and liquid samples were withdrawn and analyzed by mass spectrometer. These data are contained in Table III, page 26, and are shown graphically in Figure 9, A and A', page 27.

An important consideration in the operation of a hydrocarbon trap is to make sure that no solids are formed; under the conditions of these experiments, none were observed.



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TABLE III  
EQUILIBRIUM PHASE RELATIONSHIPS OF THC GAS - EXPERIMENTAL DATA  
INLET GAS

	Preliminary Trap at 275 p.s.i.a.				Second Equilibrium Cell at 275 p.s.i.a. <sup>d</sup>						Second Equilibrium Cell at 150 p.s.i.a. <sup>e</sup>	
	-80° F.	-100° F.	-120° F.	-140° F.	-160° F.	-180° F.	-200° F.	-220° F.	-240° F.	-250° F.	-250° F.	-260° F.
Methane (V) <sup>a</sup>	75.6	77.3	77.7	78.0	77.7	70.6	44.3	25.7	13.3	10.6	18.4	12.7
(L) <sup>b</sup>	24.7	26.3	32.8	49.4	70.7	88.8	82.0	79.6	78.6	78.3	79.1	79.5
(K) <sup>c</sup>	3.061	2.939	2.369	1.579	1.099	0.7950	0.5402	0.3229	0.1692	0.1354	0.2326	0.1597
Ethane (V)	5.3	4.2	2.9	1.6	1.2	0.2	0.1	0.1	Trace <sup>f</sup>	0.1	0.3	0.6
(L)	21.3	24.4	26.0	25.3	22.2	3.5	2.3	1.6	1.6	1.6	1.9	1.5
(K)	0.249	0.172	0.112	0.0632	0.0540	0.0571	0.0435	0.0625	-	0.0625	0.158	0.400
Ethane- (V)	6.8	4.6	3.4	1.8	1.3	0.2	0.2	0.2	Trace <sup>f</sup>	0.1	0.5	0.7
Plus (L)	73.5	73.3	67.0	49.7	27.0	4.4	2.6	1.7	1.9	1.8	2.5	1.6
(K)	0.0925	0.0627	0.0507	0.0362	0.0481	0.0454	0.0769	0.118	-	0.055	0.200	0.438
Nitrogen (V)	16.7	17.1	18.0	19.2	20.0	27.5	48.9	48.5	36.0	29.9	48.2	40.0
(L)	1.8	0.4	0.1 <sup>g</sup>	0.8	2.3	6.8	15.1	18.4	19.2	19.8	18.4	18.9
(K)	9.278	42.75	-	24.00	8.696	4.044	3.238	2.636	1.875	1.510	2.620	2.116
Helium (V)	0.9	0.9	0.9	0.9	1.0	1.7	6.7	25.5	50.6	59.4	32.8	46.7
(L)	0.006	0.004 <sup>g</sup>	0.002 <sup>g</sup>	0.009	0.008	0.047	0.102	0.172	0.191	0.171	0.058	0.077
(K)	150.0	-	-	102.3	128.2	36.6	65.4	148.3	265.2	347.0	561.6	604.9
Percent Condensed	8.87	11.80	15.47	23.60	0.84	37.09	85.77	96.21	98.17	98.43	97.08	97.75

a Mole percent composition, vapor phase

b Mole percent composition, liquid phase

c Equilibrium vaporization coefficient, V/L

d Second equilibrium cell at 275 p.s.i.a. fed by equilibrium vapor from preliminary trap held at -140° F. and 275 p.s.i.a. (data Column 4)

e Same as d except that second equilibrium cell is at 150 p.s.i.a.

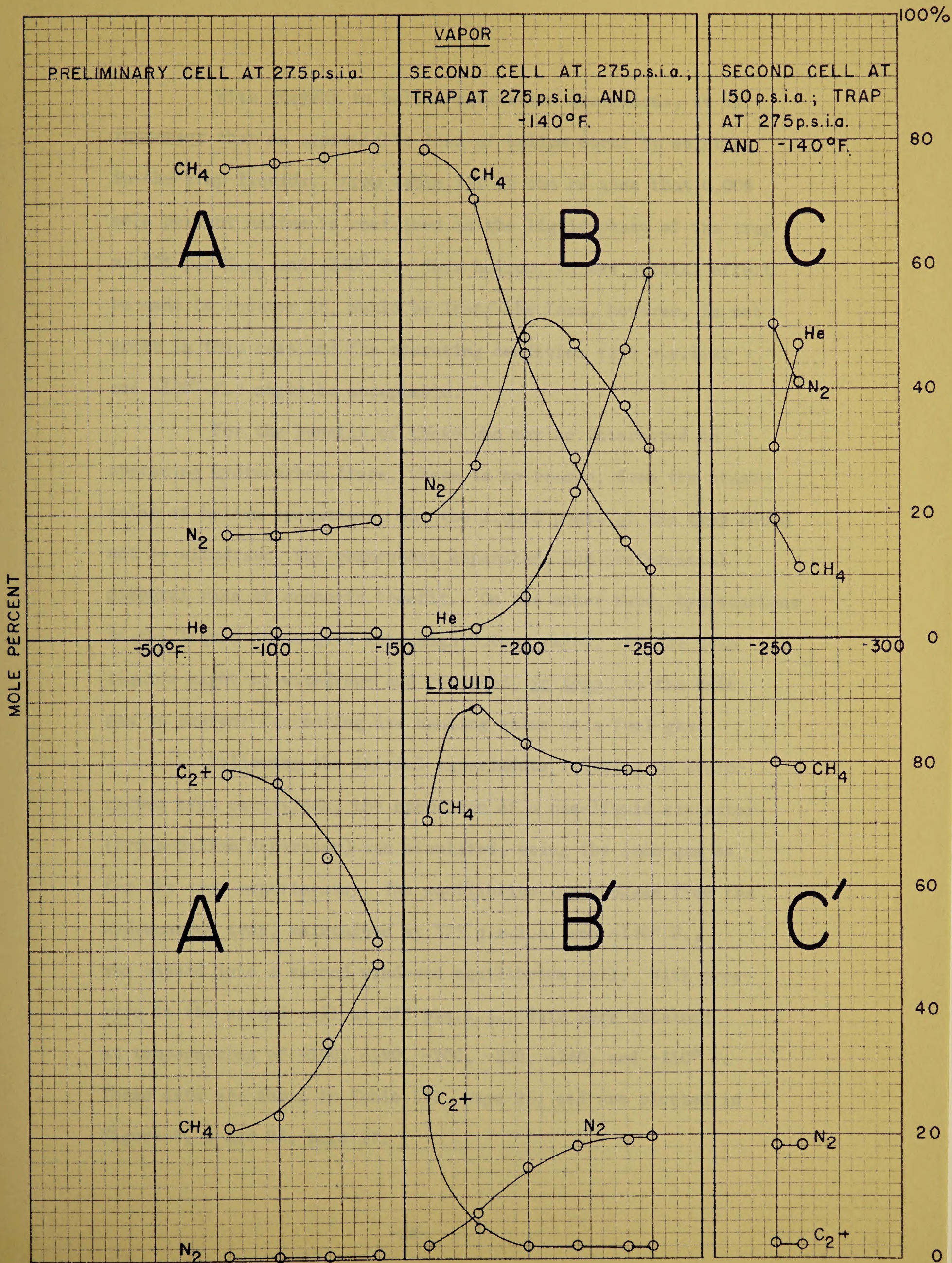
f Less than 0.05 percent

g These values are of questionable accuracy











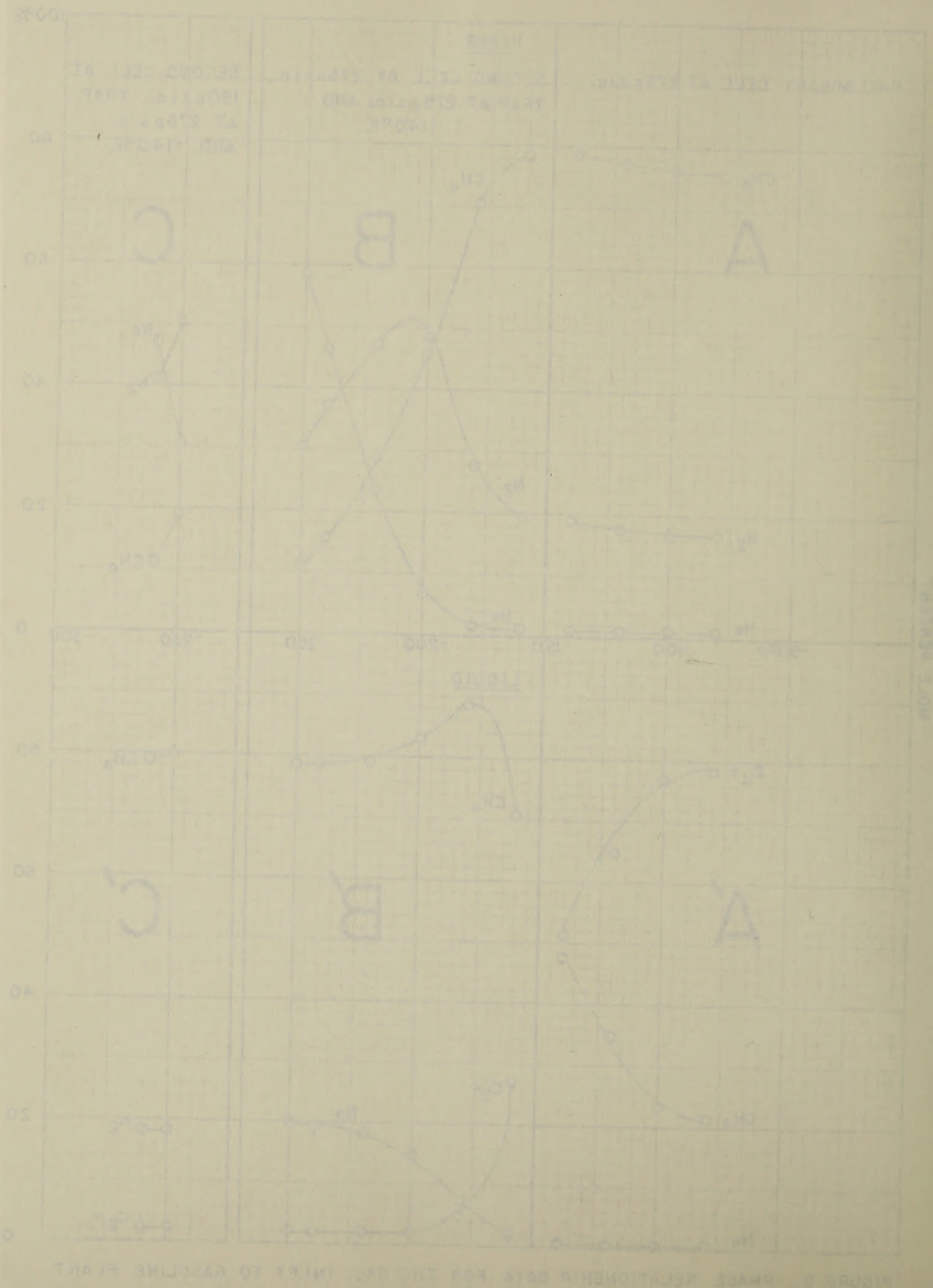


FIGURE 9. PHASE RELATIONSHIPS DATA FOR THE GAS-LIQUID SYSTEM



With respect to helium-extraction operations, it is important that no appreciable loss of helium occur by solution in the trap liquids. From Table III it can be seen that 0.009 mole percent helium is contained in the liquid phase of the trap at 275 p.s.i.a. and  $-140^{\circ}$  F. This helium, unless special effort be made to recover it, would be lost; the loss, however, is not great in this case and the operating condition (275 p.s.i.a. and  $-140^{\circ}$  F.) might be acceptable.

For the benefit of those who may be interested in operating hydrocarbon traps, there is no reason, from the standpoint of helium operations, why the liquid phase of the trap could not be withdrawn, the components separated, and preferential disposal made at economic benefit. On the other hand, hydrocarbons in the liquid phase give it a high B.t.u. value, and the trap liquids might be withdrawn and returned, in toto, to the exit gas to prevent decreasing its heating value as a fuel gas.

Following the initial experiments relating to hydrocarbon trap conditions, the operation of a gas-liquid separator (crude-helium separator) was simulated, using the same gas as for the trap experiments. The equilibrium vapor phase from the hydrocarbon trap, maintained at 275 p.s.i.a. and  $-140^{\circ}$  F., was passed into a second windowed equilibrium cell. With pressure in the second cell at 275 p.s.i.a., data were obtained at temperatures of  $-160$ ,  $-180$ ,  $-200$ ,  $-220$ ,  $-240$ , and  $-250^{\circ}$  F. These data are shown in Table III, page 26, and are plotted in Figure 9, B and B', page 27.







Assuming the second equilibrium cell to represent the crude-helium separator in a typical helium-extraction process, one might suppose, from an examination of Figure 9B, that the best operating conditions for this unit would be those at which the percent helium in the vapor was greatest.

Such a supposition is not necessarily correct, because at this stage of helium production, the percentage helium in the vapor is not as important a consideration as the solubility of helium in the liquid phase. Data concerning helium solubility are not plotted in Figure 9B because the scale is inappropriate; these data are, however, contained in Table III, page 26. Here it may be noted that at 275 p.s.i.a. and  $-250^{\circ}$  F., (where the maximum percent helium in the vapor is obtained) the mole percent helium in the liquid phase is 0.171.

At these conditions of pressure and temperature, the gas is 98 percent condensed (see Figure 10, page 30). Therefore, the 0.171 mole percent helium in the liquid represents

$\frac{(.171)(.98)}{.75}$ , or 21 percent of the helium contained in the feed gas. Expressed in another way, if the dissolved helium were not recovered, the extraction efficiency could not possibly exceed 79 percent. The efficiency at plants now in operation exceeds this figure. To increase efficiency, helium in solution might be "stripped" out of the liquid and recovered by conventional methods. This would become increasingly desirable with lower concentrations of helium in the feed gas. Figures 9C and C' show data obtained in a crude-helium separator operated



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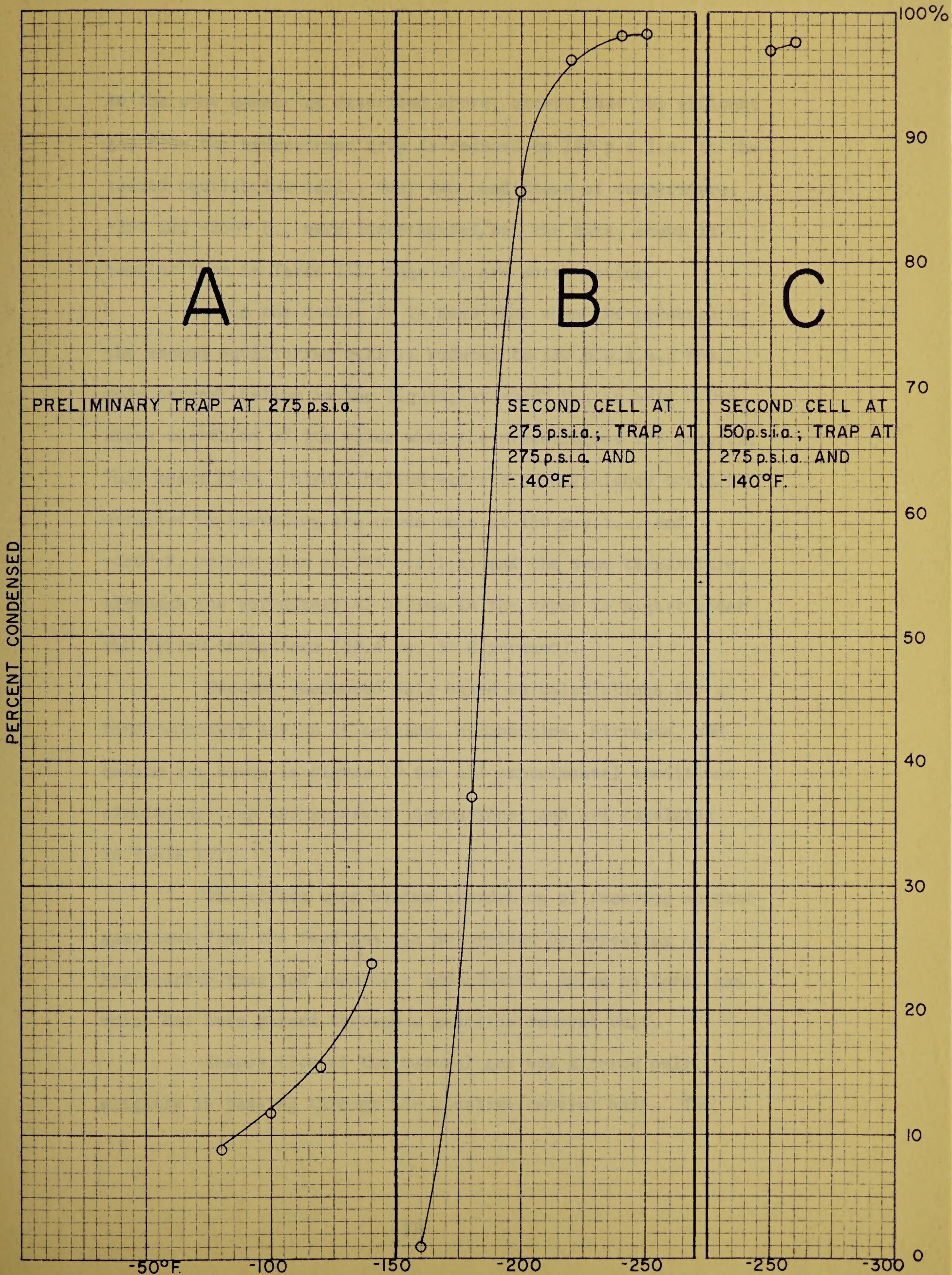
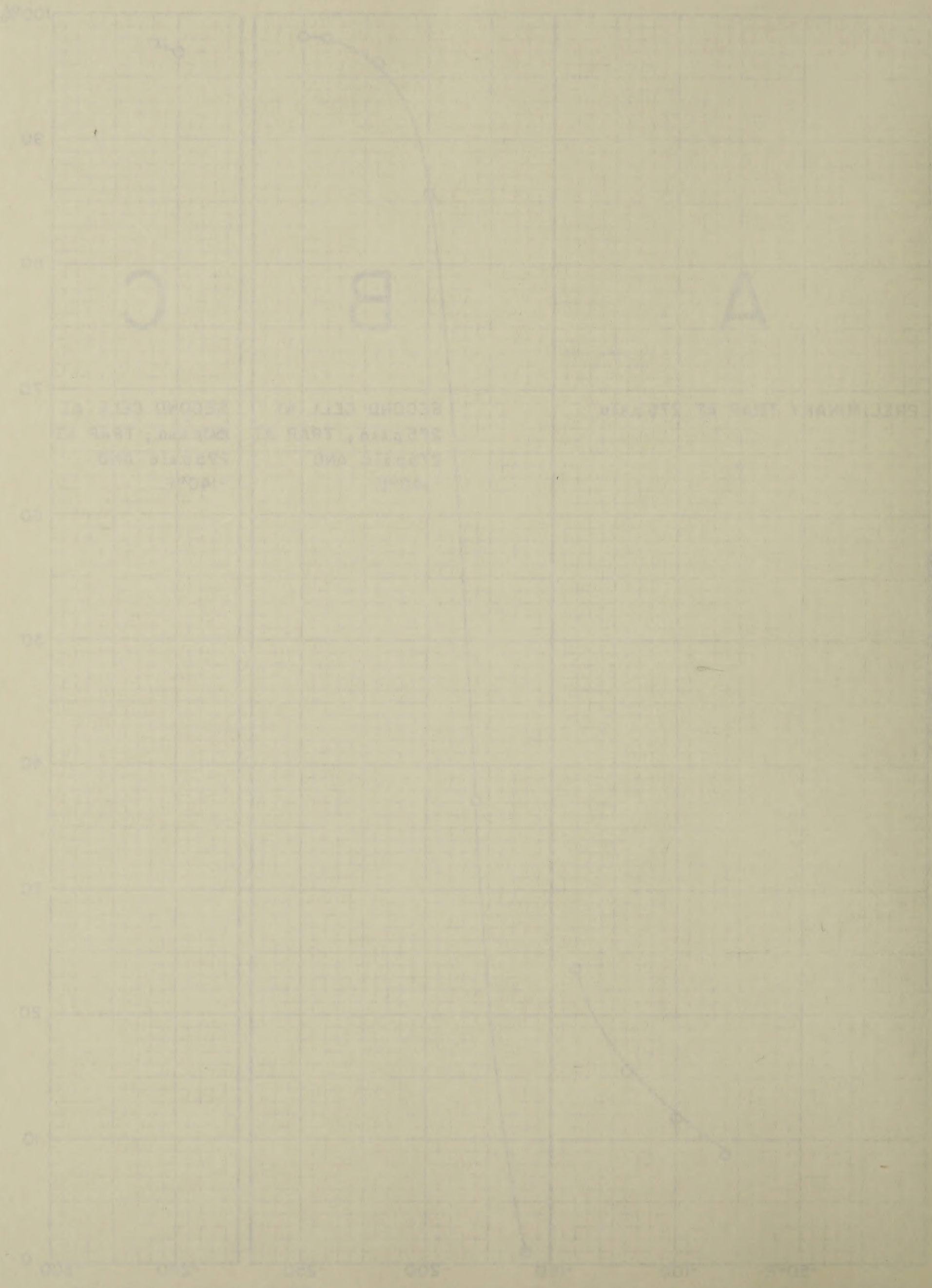


FIGURE 10. PERCENT CONDENSED DATA FOR THC GAS, INLET TO GASOLINE PLANT





PRELIMINARY DATA AT STEADY STATE

FIGURE 10. PRELIMINARY DATA AT STEADY STATE, INLET TO GASOLINE PLANT



in the same manner as described above, except that the effluent gas from the hydrocarbon trap is reduced to 150 p.s.i.a. in the second equilibrium cell. Only two conditions of temperature, -250 and -260° F., were investigated, but the data, shown in tabular form in Table III, page 26, are worth noting.

From the table, it is seen that when the pressure in the second equilibrium cell is reduced to 150 p.s.i.a., the mole percent helium in the liquid, at -250° F., is only 0.058, about one-third of its value when the pressure was 275 p.s.i.a. This means that a higher helium-extraction efficiency could be obtained by operating the crude unit at 150 p.s.i.a. and -250° F. rather than at 275 p.s.i.a. and the same temperature, although the percentage of helium in the vapor is higher under the latter conditions (59.4 vs. 32.8 percent).

Percent condensed data based on calculations for a four-component system of methane, ethane-plus, nitrogen, and helium are shown in Figure 10 for all experimental conditions simulating trap and separator operations, and are tabulated in Table III.

The effect upon helium extraction of removing natural gasolines from the feed gas was determined by repeating the hydrocarbon trap and separator experiments, using as feed, gas which had been passed through a gasoline removal unit.

Composition of the natural gas was altered only slightly in passing through the gasoline removal unit. The







methane concentration increased approximately 1.5 mole percent, propane decreased one percent, n-butane decreased 0.7 percent, and pentanes and heavier components were removed completely. The nitrogen content increased about one percent and the loss of helium in the gasolines was negligible.

For the benefit of those who may be interested in noting the results of trap and separator experiments conducted with the outlet gas from a natural gasoline removal unit, the data are shown in Table IV, page 33, and in Figures 11 and 12, pages 34 and 35. These data should be considered in the same manner as for the inlet (THC) gas.

In summarizing the work done in this investigation it should be borne in mind that the data were obtained under expeditious conditions. A more complete phase relationship study of this gas has been scheduled and publication is anticipated. Nevertheless, the information contained in the present report should be of definite value to those interested in vapor-liquid data for natural gases similar in composition to those they may process if they participate in the Helium Conservation Program.







TABLE IV  
EQUILIBRIUM PHASE RELATIONSHIPS OF A THC GAS - EXPERIMENTAL DATA  
OUTLET GAS

			Preliminary Trap at 275 p.s.i.a.				Second Equilibrium Cell at 275 p.s.i.a. <sup>d</sup>					Second Equilibrium Cell at 150 p.s.i.a. <sup>e</sup>	
			-80° F.	-100° F.	-120° F.	-140° F.	-160° F.	-180° F.	-200° F.	-220° F.	-240° F.	-250° F.	-260° F.
Methane	(V) <sup>a</sup>		75.4	76.3	77.5	76.4	78.1	70.4	45.4	28.9	15.6	11.0	19.0
	(L) <sup>b</sup>		21.3	22.9	35.2	47.9	70.7	88.4	82.8	79.3	78.8	78.9	79.8
	(K) <sup>c</sup>		3.540	3.332	2.202	1.595	1.105	0.7964	0.5483	0.3644	0.1980	0.1394	0.2381
Ethane	(V)		5.7	5.5	3.6	2.2	1.2	0.3	0.1	0.2	0.1	0.2	0.1
	(L)		22.0	28.9	31.8	28.5	23.7	4.3	2.1	2.5	1.8	1.8	0.4
	(K)		0.259	0.190	0.113	0.0772	0.051	0.070	0.048	0.080	0.056	0.111	1.9
Ethane Plus	(V)		7.0	5.3	4.0	2.3	1.2	0.3	0.1	0.2	0.2	0.2	0.1
	(L)		78.0	76.9	64.7	51.3	27.3	4.8	2.3	2.7	2.1	1.9	0.4
	(K)		0.0897	0.0819	0.0618	0.0448	0.0439	0.0625	0.0435	0.0741	0.0952	0.1051	2.1
Nitrogen	(V)		16.8	16.4	17.7	20.3	19.7	27.7	48.1	47.7	37.4	30.0	50.4
	(L)		0.0	0.1 <sup>f</sup>	0.0	0.5	1.8	6.7	14.9	17.8	18.9	19.0	18.2
	(K)		-	-	-	40.60	10.94	4.134	3.228	2.680	1.979	1.579	2.769
Helium	(V)		0.8	0.8	0.8	1.0	0.9	1.6	6.4	23.3	46.8	58.8	30.4
	(L)		0.002 <sup>f</sup>	0.002 <sup>f</sup>	0.007	0.007	0.009	0.009	0.068	0.151	0.183	0.188	0.079
	(K)		-	-	114.3	142.9	100.0	177.8	94.1	154.3	255.7	312.8	384.8
Percent Condensed			4.67	5.31	11.64	15.97	3.80	37.36	84.53	95.73	98.16	98.57	97.36
													98.27

a Mole percent composition, vapor phase

b Mole percent composition, liquid phase

c Equilibrium vaporization coefficient, V/L

d Second equilibrium cell at 275 p.s.i.a. fed by equilibrium vapor from preliminary trap held at -140° F. and 275 p.s.i.a. (data Column 4)

e Same as d except that second equilibrium cell is at 150 p.s.i.a.

f These values are of questionable accuracy







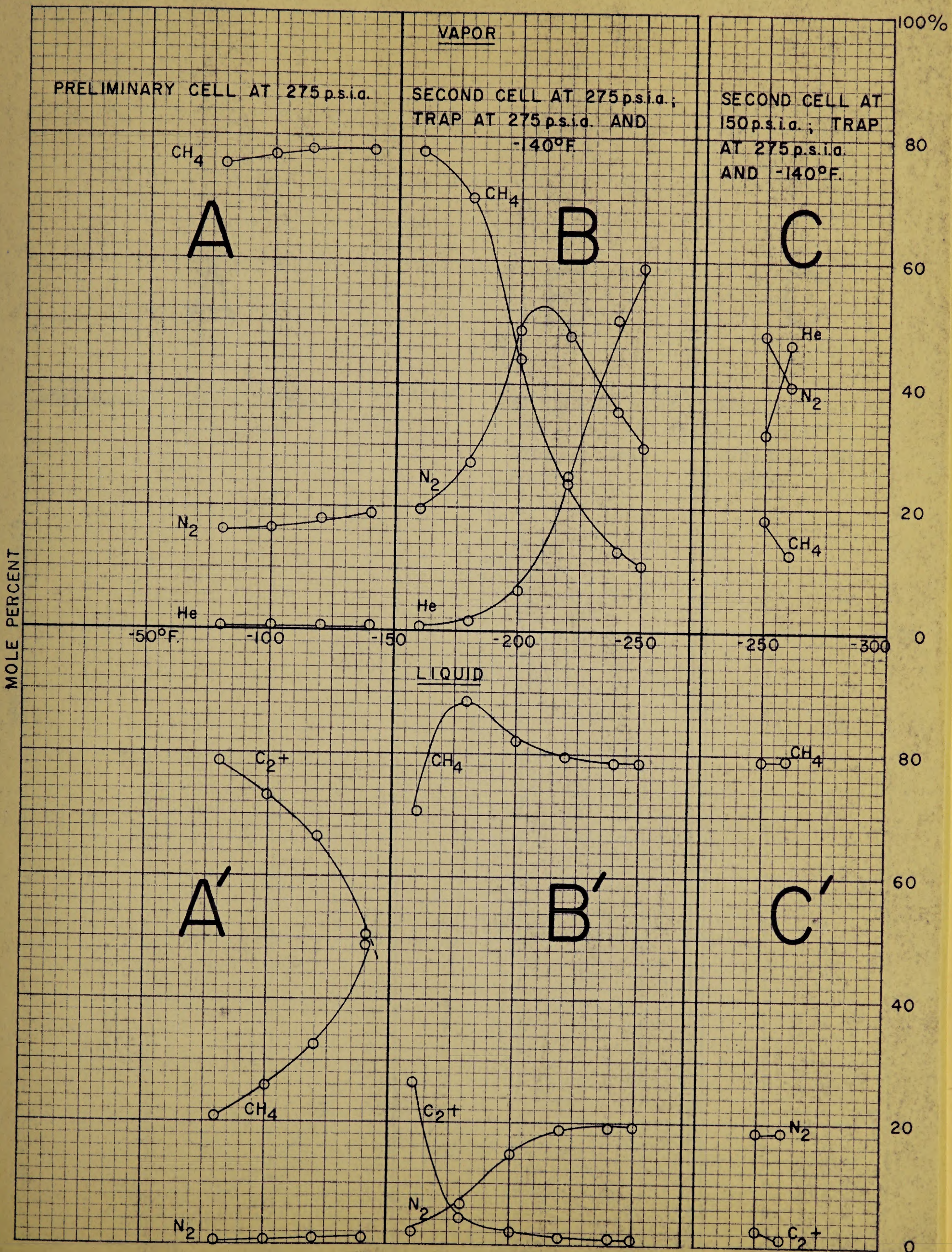


FIGURE II. PHASE RELATIONSHIP DATA FOR THC GAS, OUTLET FROM GASOLINE PLANT





FIGURE 11. PHASE RELATIONSHIP DATA FOR THE GAS OUTLET FROM CASUALTY PLANT



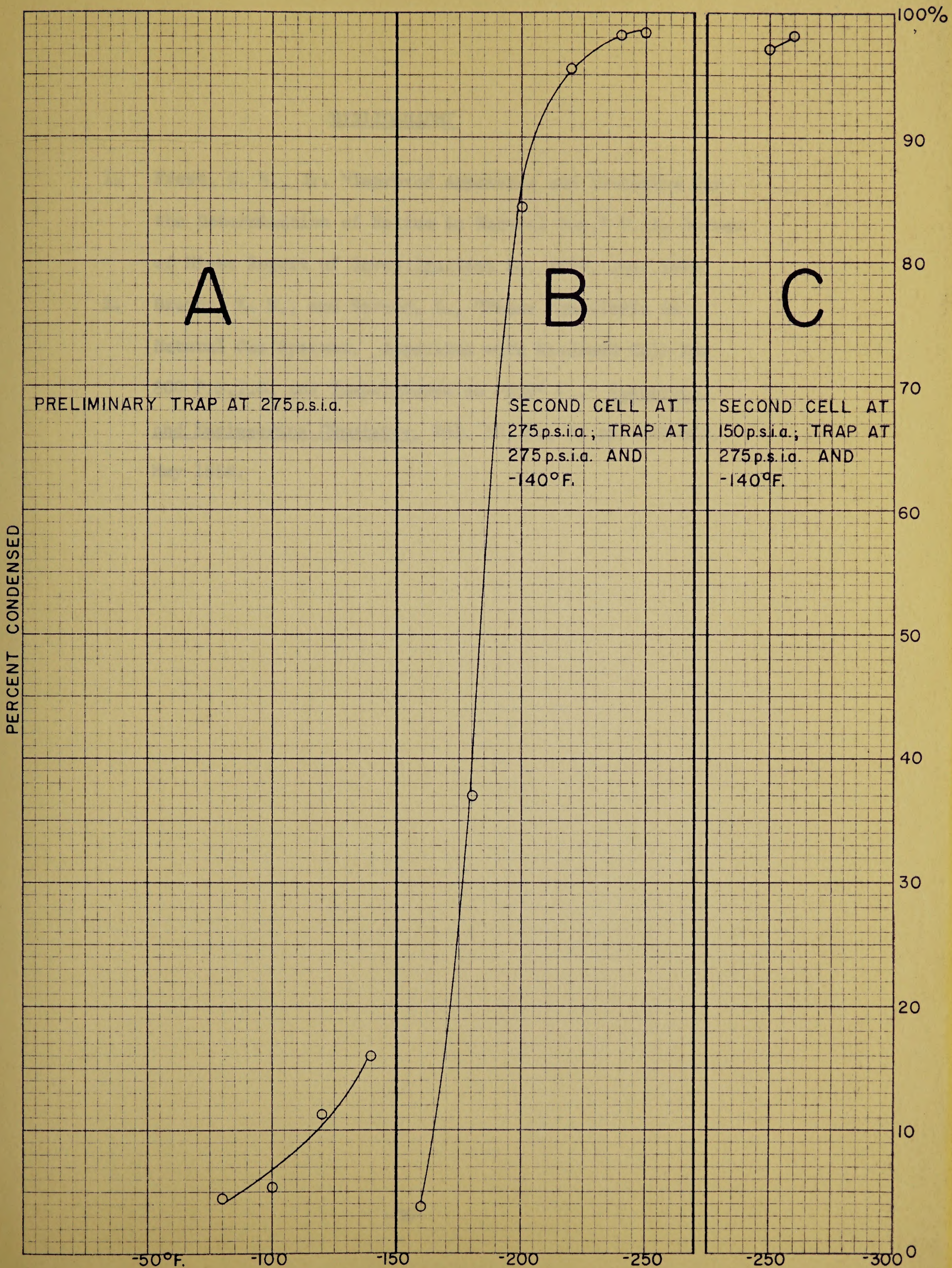


FIGURE 12. PERCENT CONDENSED DATA FOR THC GAS, OUTLET FROM GASOLINE PLANT



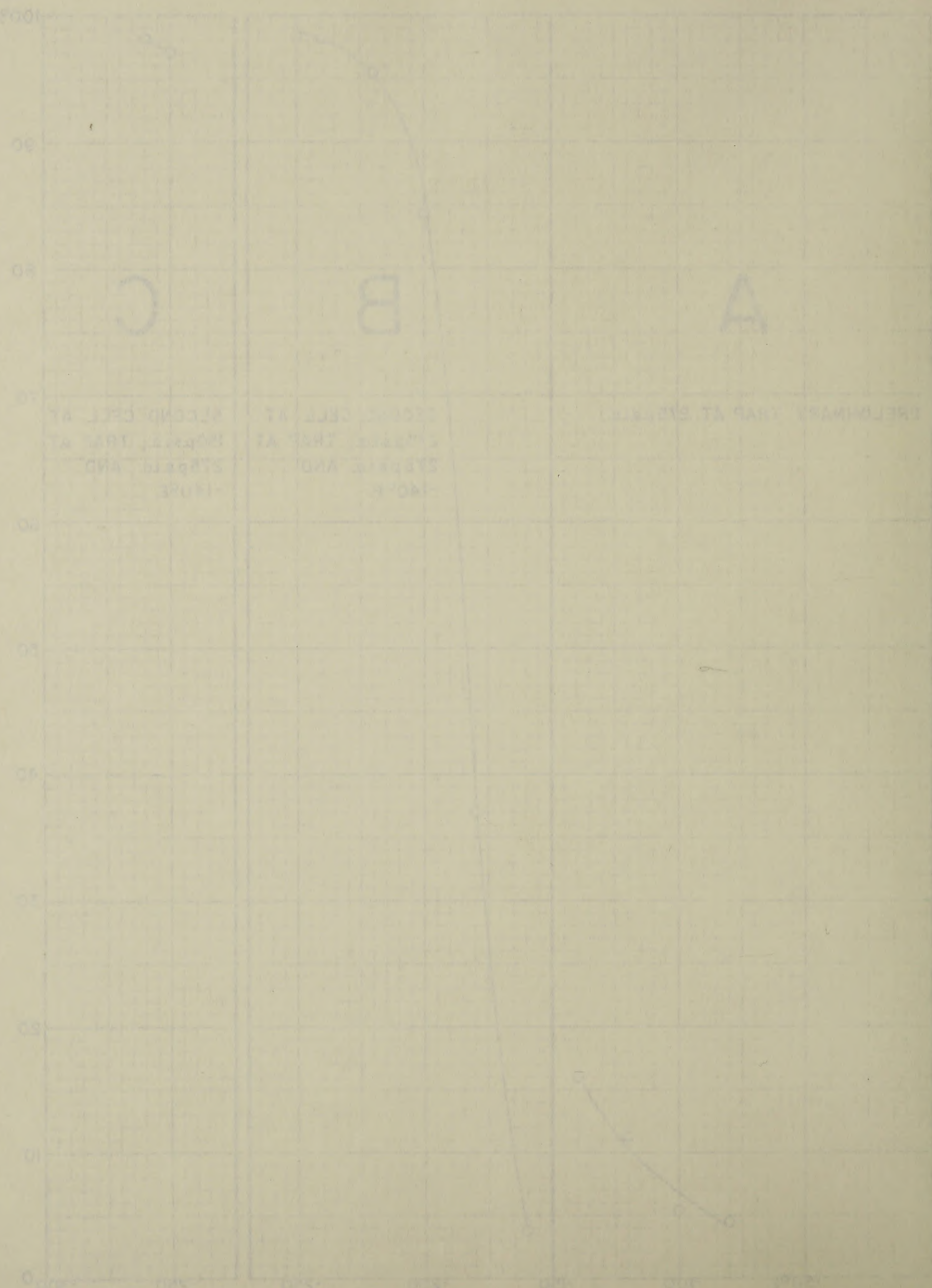


FIGURE 1. A COMPARISON OF THE DATA FOR THE TWO CASES.



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THE JOURNAL

1. The first of the three main parts of the book is devoted to a general survey of the history of the subject. The second part is devoted to a detailed study of the various theories of the origin of the subject. The third part is devoted to a study of the various theories of the development of the subject.















